

## Review

# Biodiesel via supercritical ethanolysis within a global analysis “feedstocks-conversion-engine” for a sustainable fuel alternative



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## ABSTRACT

The challenges in reducing the world's dependence on crude oil and the greenhouse gas accumulation in the atmosphere, while simultaneously improving engine performance through better fuel efficiency and reduced exhaust emissions, have led to the emergence of new fuels, with formulations blending petrodiesel, biodiesel, bioethanol and water in various proportions. In parallel, the sustainability of the new biofuel industries also requires to maintain a high level of biodiversity while playing on techno-diversity, using a variety of resources that do not compete with edible crops (nor by using arable land for energy crops or food crops for energy production) and flexible conversion technologies satisfying the eco-design, eco-energy and eco-materials criteria. In addition, it would be relevant to consider blending ethyl biodiesel, instead of methyl biodiesel, with petrodiesel, particularly if the fuel formulation is completed with bioethanol (or even water). The supercritical ethanolysis of lipid resources to produce ethyl biodiesel is a simple but efficient route that should have the potential to satisfy the sustainability criteria if analyzed holistically. Therefore, this review focuses specifically on the production of ethyl biodiesel via triglyceride supercritical ethanolysis within a global analysis “feedstocks-conversion-engine”. The scientific and technical bottlenecks requiring further development are highlighted by emphasizing (i) the kinetic and thermodynamic aspects (experiments and modeling) required for the process simulation, the results of which aim at securing the life cycle assessment, first at the process level and then at the fuel level; (ii) the proposals to improve the supercritical process performance in terms of eco-material and eco-energy; (iii) the impacts of ethyl vs. methyl biodiesel fuels and of biodiesel–ethanol–petrodiesel blends (with or without water) on the diesel engine emissions and performance; (iv) the technological flexibility of the supercritical process allowing its conversion toward production of other key products. Finally, built on the state-of-the art review, a new R&D direction combining supercritical ethanolysis of lipids with the addition of CO<sub>2</sub>, glycerol recovery, and cogeneration, according to the biorefinery concept, is proposed and discussed.

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## 1. Introduction

Having approved the “Climate and Energy Package” aiming at a sustainable security of energy supply, and the commitments on climate change, the European Council adopted two directives on biofuels (2009/28/EC and 2009/30/EC) setting targets for the next ten years, to which have been added two new emission standards (Euro 5 and Euro 6).

The European Directive 2009/28/EC aims to achieve by 2020 a 20% share of renewable energy (RE) in the final energy consumption in the EU and a 10% share of renewable energy consumption in each Member State for the transport sector alone, currently 96% dependent on oil. Internal combustion engines are still dominant in this sector. This objective is thus equivalent to

almost a 10% share of biofuels in overall transport fuel consumption. In addition, this Directive defines the sustainability criteria that biofuels must meet, in particular those regarding greenhouse gas (GHG) emissions and biodiversity. Concerning the GHG ( $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{NO}_2$ ), significant reductions must be met during their use (at least 35% by 2011, 50% in 2017) and the entire life cycle of biofuel from crop or extraction to combustion (2020: 6% reductions in GHG emissions compared to the energy produced in 2010 from fossil fuels). In terms of biodiversity, a restriction on the use of land for biofuel production is also planned, excluding high biodiversity value land and land with high carbon storage [1,2]. The European Directive 2009/30/EC sets fuel specifications and incorporates the sustainability criteria for biofuels in defining the methodology for calculating GHG emissions from

biofuels throughout their life cycle, from cultivation or extraction to combustion [1,3].

The Euro 5 emissions standard for passenger cars, in force since September 2009, establishes new vehicle emission pollutant levels (generated during fuel combustion) even stricter than Euro 4. For vehicles with diesel engines, these levels were reduced by 28% for nitrogen oxides (NO<sub>x</sub>), 80% for particulate matter (PM) and 23% for the total hydrocarbons (HC) & NO<sub>x</sub>. Only carbon monoxide (CO) had his tolerance limit unchanged. The Euro 6 standard planned for September 2014 applies an additional reduction of over 50% for NO<sub>x</sub> and 26% for HC & NO<sub>x</sub> [4].

Due to their properties, similar to those of conventional fuels, and their renewable character, bioethanol and biodiesel are judicious biofuel candidates for the partial substitution of gasoline and diesel, respectively [5–7].

In the EU the biodiesel consumption is more than four times higher than ethanol (in energy terms), with an increase of 11% since 2008. This strong demand for biodiesel in the EU is due to a large diesel transport fleet, a trend that was reversed from 2007 but that has been on rise again since 2010 [5,8–11]. However, the major routes of industrial production of bioethanol and biodiesel present weaknesses. The biofuels currently marketed, the so-called first generation (1G), are mainly produced from “edible” biomass (sugar plants and grain for bioethanol, and oilseeds (rapeseed, soybean) for biodiesel), the actual problem being that these food crops are often directly used to produce these biofuels. For example in 2010, about 40% of the tonnage of maize produced in the U.S. [12] and less than 5% of the production of cereals and sugar beets in France were used to make bioethanol [13]. The situation is more complex for sugar plants as bioethanol can be produced directly from them but also from the spent molasses from the edible sugar production (11% of the sugar beets produced in France are used directly for bioethanol production [14]). These resources are then subjected to a conversion based on mechanical changes, biochemical or chemical transformation and, finally, thermal. In the production of biodiesel, in addition to triglycerides (TG) derived from oilseeds, an alcohol, usually methanol, is also used. These biofuel pathways present therefore a major constraint which restricts their sustainable development: the limited agricultural biomass resource. This leads to a dangerous competition with agricultural production for food, and also to a negative environmental footprint with deforestation in some areas of the globe, causing a reduction in biodiversity, and a displacement of the pollution (CO<sub>2</sub> reduction through plant photosynthesis, offset by pollution-induced at soil–water during the agricultural exploitation of resources (by fertilizers) and their conversion into biofuel (with generation of effluents)) [15,16]. As a result of these negative impacts induced by the indirect land use change (ILUC) of 1G-biofuels, the European Commission have recently proposed a 5% limitation in the amount of 1G-biofuels that can be accounted toward the EU’s 10% target for renewable energy in the transport sector by 2020 [17,18]. Thus, the diversification both in terms of resources, their origin, and the conversion technologies applied is the basis to secure a long-term supply of biofuels, while allowing them to meet the sustainability criteria [11,19,20]. Conversion technologies with the flexibility to easily adapt to context (in terms of both chemicals, and geographical location) are additional criterion for sustainability.

### 1.1. Main objectives

This review focuses specifically on the production of biodiesel fuels by supercritical (Sc) TG ethanolysis within a global analysis “feedstocks-conversion-engine”. The targeted biodiesel fuels are dedicated to common transportation vehicles (cars, trucks) as well as power generators; indeed, biodiesels are currently not

considered viable aviation fuels which require synthetic hydrocarbon fuels obtained by other technologies, such as hydrodeoxygenation processing of natural oils and fats, or Gas-to-Liquid synthesis by Fischer–Tropsch process [21,22]. The main reasons for this choice are: (i) the absence of catalyst that makes this approach environmentally friendly, very flexible in the use of feedstocks (having no limitations of acidity or water content), and allows a simplification and reduction in the process equipment; (ii) the alcohol, i.e. bioethanol, is a non-toxic, biodegradable, and green raw material when produced from non-edible biomass residues, leading to a 100% renewable biodiesel; (iii) the enlarged analysis of the alternative biodiesel, from cradle to grave, which considers that performances of new-generation fuels depend on the feedstocks, the conversion process and the engine emissions, and that all these aspects need to be analyzed together. In line with the integrated approach “life cycle fuel” & “sustainability criteria”, advocated by the European directives 2009/28/EC and 2009/30/EC, such global approach has positive features among which:

- Taking exhaustively into account the drawbacks and advantages of the technology within its ultimate purpose, i.e. the conversion of low-cost feedstocks in high quality biofuel while minimizing environmental and economical impacts and maximizing energy and material efficiencies. This integrated evaluation method should lead to more reliable conclusions on the sustainability of alternative fuels when the feedstocks and their conversion process are considered together, along with the engine emissions.
- Supporting the use of computational tools, integrating kinetic and thermodynamic models, in order to optimize the selection of feedstocks and the conversion process variables (design and operating conditions) toward the production of fuels with specific combustion properties while meeting the sustainability criteria along the entire chain.

Recent studies regarding life cycle assessment (LCA) of biofuels [23,24] have followed this global approach. In the same line, Anitescu and Bruno [25] proposed a new conceptual design of *in situ* generation of biodiesel fuel via Sc-TG transesterification coupled with Sc fuel injection and combustion. The authors also reviewed the fluid properties required for both production and combustion of biodiesel fuel via the supercritical technology.

### 1.2. Main highlights

A number of reviews on the different routes of biodiesel production were published recently [5,9,26–31], for various classes of feedstocks [5,9,20,26,28,30–37], with ethanol to replace methanol as alcohol [6,29] (these citations are not exhaustive lists). Nevertheless, very few reviews are focused on the supercritical biodiesel production. Among the few those by Sawangkeaw et al. [38], Boer and Bahri [39], and Anitescu and Bruno [25] are the most relevant.

Complementary to these works, the present review is dedicated to the TG supercritical ethanolysis, and thus to ethyl biodiesel production. Nevertheless, most of the research in the literature has been developed by using methanol as reactant. Therefore, the manuscript illustrates the supercritical transesterification via methanolysis, and then discusses the supercritical ethanolysis vs. methanolysis by highlighting the specific features. Moreover, to highlight the existing scientific and technical bottlenecks requiring further development, this work emphasizes:

- (i) the kinetic and thermodynamic models that are required for conducting a reliable process simulation, the results of which aim at securing the LCA related to the process;

- (ii) the experimental information needed to evaluate or develop, if necessary, the kinetic and thermodynamic models;
- (iii) the diesel engine emissions and performance of ethyl vs. methyl biodiesel fuels;
- (iv) the proposals made to improve the performance of the supercritical method;
- (v) the technological flexibility of the supercritical route, allowing the conversion of the process toward the production of other key products (e.g. bio-sourced monomers);
- (vi) the methodologies to assess a fuel alternative more equitably (by including its production and combustion).

Impacts of biodiesel–ethanol–petrodiesel blends (with or without residual water) on diesel engine performance and emissions are also discussed at the macroscopic scale similarly to an input–output material balance, while mechanistic interpretations can be found in specific literature reviews focused on combustion chemical kinetics of biofuels [40–43]. If these impacts are positive, residual water and ethanol in biodiesel may be beneficial to reduce the overall GHG footprint of the fuel, not only at the engine level but also at the production stage by avoiding some energy intensive purification processes. Finally, built on the state-of-the art review, a new R&D direction is proposed and discussed.

## 2. Supercritical ethanolysis of TG: a new technology to convert a new generation of feedstocks into a new generation of biofuels

Based on the knowledge acquired during the development of the 1st generation biodiesel and bioethanol, 2nd generation (2G) biofuels using only non-edible resources such as lignocellulosic biomass (wood, grass, straw ...) appeared [5,23,44–47]. These are converted either by hydrolysis followed by fermentation for bioethanol production, or by gasification followed by Fischer–Tropsch (FT) conversion, in a process known as Biomass-to-Liquid (BtL) to produce FT-diesel. These 2nd generation biofuels, developed based on the biorefinery concept that aims at using the whole biomass for a variety of applications (energy carriers, heat and power generation, or green chemistry with specialty of chemicals and materials), involve a reduced use of water and agrochemicals when compared with the 1st generation (1G) biofuels. Nevertheless tensions may occur related with soil occupation or the use of genetically modified organisms (GMO) in the case of uncontrolled development of dedicated cultures [5]. Therefore, a large range of new resources, focusing on the diversification and availability, have been proposed.

### 2.1. New-generation feedstocks 2G&3G

The lipid feedstocks of 2nd- and 3rd-generation (2G&3G) which can be converted successfully by supercritical alcoholysis (ethanolysis but also methanolysis) are briefly mentioned in this section. Further details on these feedstocks are available in various articles and literature reviews recently published [5,20,30,33–36,48–52] (this is not an exhaustive list). Converting the 2G&3G lipid feedstocks via a thermochemical route, the Sc-method is based on a hybrid process leading to 2G&3G biodiesels.

#### 2.1.1. Non-edible vegetable oils

*Jatropha curcas* (Jatropha) and *Pongamia pinnata* (Karanja), adapted to arid soils unsuitable for food crops, and producing non-edible vegetable oils (NEVO) with yields of 2000 L/hectare annum, well above those of canola or soy, have been developed and successfully used for biodiesel production [49,50,53–55]. The remaining parts of the plant may found application in the production of fertilizers, pesticides and drugs. Their culture may also

prevent the soil erosion [5,56–58]. Many other NEVO have been proposed as potential candidates to biofuel production [20,35,36]. Some seem to grow without any care such as *Balanites aegyptiaca* (Desert date) [59], while others such as *Azadirachta indica* (Neem) [60], *Pistacia chinensis* Bunge [61], or *Amygdalus pedunculata* [62] were also identified reinforcing the biodiversity and availability of the resources. These NEVO may become the basis for an energetic autonomy of emerging countries, provided that the technology of conversion into biofuels may be adequately adapted [63,64].

#### 2.1.2. Residues and waste from biomass

The use of “residual and waste” biomass is strongly encouraged by the 2009/28/EC and 2009/30/EC European directives, with specific measures taking into account the intrinsic sustainability of these resources. In fact, 65–95% of the total production cost of biodiesel is due to the raw materials employed [65,66]. These may be forest and agricultural residues (molasses, and grape marc residue or sugarcane bagasse) or agro-food waste (waste cooking oil (WCO) consisting mainly of frying oils and smaller proportion of animal fats, and waste fish oils (WFO) among others). These are seen as generating 2G biofuels, regardless of the processing technology used. Biodiesel production from WCO to replace plant edible oils has led in recent years in Japan, Spain and France, among other, to the creation of collecting societies [67]. The total production of WCO in Japan is estimated at between 0.45 and 0.57 million tons/year, 0.7–10 million tones/year in the EU, and 10 million tons/year for the United States [31]. This sector is therefore a resource pool of interest, especially as their use is virtually carbon neutral because all carbon dioxide released in their production can be attributed to their original food use [68].

#### 2.1.3. Algal biomass

Algal biomass (micro-and macroalgae), still at the research stage, would be a very promising way of producing third generation (3G) biofuels, such as biohydrogen [34,48], biomethane [48,52], bioethanol [37,48,69] or biodiesel [34,37,52,70] depending on the variety of seaweed used [5,34,37,48,52,70]. The potential success of this approach depends on the diversity of existing algal resources. They may found a variety of applications ranging from food, pharmaceuticals, and cosmetics to energy. They are also highly appealing since these cultures, free from the constraints of soil, lead to high yields in resources convertible into biofuels, and may be used for CO<sub>2</sub> capture and fixation and wastewater usage [5,37,71]. However, significant limitations continue to block the development of large scale microalgae biofuel production, explaining the negative outcome of recent life cycle analyzes [72,73]. Research and development efforts are required in selecting microalgae strains specifically adapted to regional conditions, improving reactor design, and integrating processes with efficient product separation schemes, which would reduce processing costs, while increasing product yields [34,52,71,73]. The biorefinery approach will also be central to the overall feasibility of microalgal biotechnology by producing high added-value products [34,74] while potentially using wastewater and glycerol [52,75].

### 2.2. The reaction step in the process of supercritical ethanolysis of TG

Similarly to the conventional process, the conversion reaction is the transesterification (alcoholysis) of triglycerides (major constituents of oils and fats) with an alcohol to yield biodiesel with formation of glycerol. In the remainder of this work, biodiesel produced from ethanol is called “ethyl biodiesel” as opposed to commercial “methyl biodiesel” produced industrially from methanol. Biodiesel and glycerol are immiscible at atmospheric pressure,



the latter being separated by decantation. The transesterification is generally carried in presence of a catalyst (acid or alkali) to accelerate the reaction, except when the alcohol reacts at the supercritical state. Being a reversible chemical equilibrium, the transesterification can be displaced toward the formation of esters by removing the glycerol from the media. This is the concept behind the industrial Henkel process, carrying the transesterification in two stages with intermediate removal of the glycerol [76].

Overall, the stoichiometry of the transesterification (ethanolysis or methanolysis according to the alcohol used, i.e. ethanol or methanol) is 1 mole of triglyceride for 3 moles of alcohol to form 3 moles of esters and 1 mole of glycerol (Fig. 1a). Nevertheless, the overall equation is the result of three consecutive reversible reactions leading to intermediate diglycerides and monoglycerides (Fig. 1b). Because of this reversibility, an excess of alcohol is normally used. Glycerides having different alkyl groups  $R_x$ , the biodiesel product is a mixture of fatty acid ethyl esters (FAEE) (or methyl esters (FAME)) with different alkyl chain lengths ( $k + m + 2$ ), and numbers of double bonds ( $n$ ) (Fig. 1).

Table 1 presents, for selected vegetable oils and fats, the average composition of fatty acids corresponding to the fragments  $R_x\text{COOH}$  with  $x = 1, 2$  or  $3$  of the triglycerides (Fig. 1a). Normally linked to the glycerol backbone under the triglyceride form, these fragments must be differentiated from the free fatty acids (FFA) that are naturally found in the lipids. As the data in Table 1 show, the more abundant fatty acids in vegetable oils are the saturated palmitic (C16:0) and stearic (C18:0) acids and the unsaturated oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids [77,78]. Animal fats (including fish oils) contain longer fatty acids (up to 22 carbon atoms) with a higher degree of unsaturation (up to 6 double bonds). Thus, the lipidic resources used as raw materials determine the FAME (or FAEE) composition of the biodiesel product.

Non-edible vegetable oils (NEVO), and particularly waste cooking oils (WCO) may contain high amounts of FFA (up to 36 wt% [79,80]), as well as water in WCO or lipids obtained from the pre-concentrated algal biomass. The presence of water and FFA may

lead, under certain conditions, to two reactions: hydrolysis of TG (Fig. 2a) and esterification of FFA (Fig. 2b).

### 3. Supercritical process – main features, key benefits, disadvantages and potential solutions

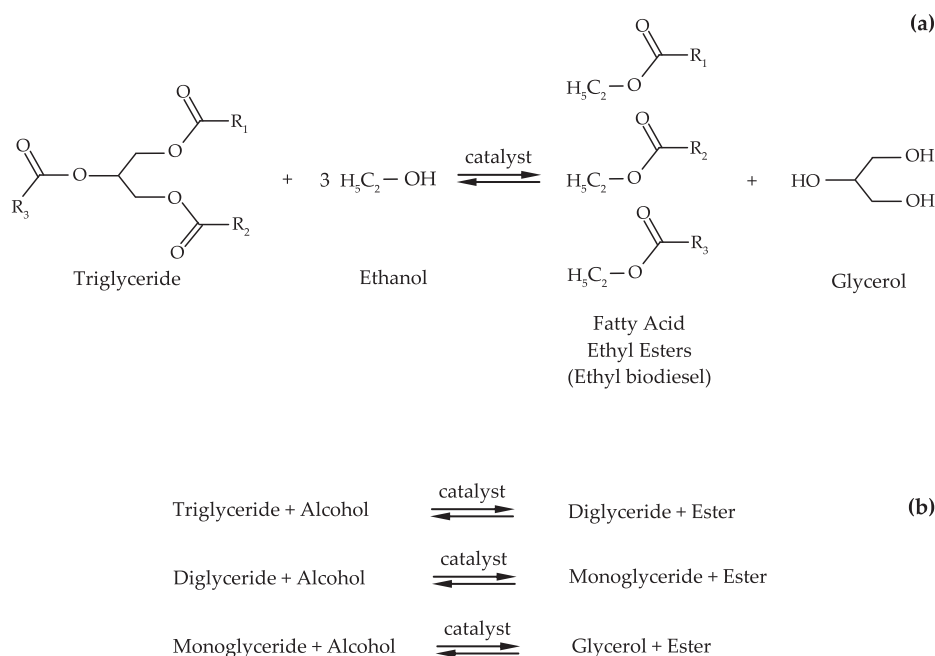
#### 3.1. Methyl biodiesel vs. ethyl biodiesel

While bioethanol has the advantage of being non-toxic and produced exclusively by biological pathways from renewable resources, methanol remains, despite its toxicity and non-renewable character, the alcohol of choice for biodiesel production. Main reasons are its lower cost and the technical difficulties associated with the change of methanol to bioethanol in a conventional process: longer reaction time, separation and purification of biodiesel and glycerol more difficult, formation of more stable emulsions and greater solubility of glycerol in ethyl esters [81–84]. When using a supercritical process without catalyst addition, the problem of emulsions is avoided. However for the same yields of 98% esters, some problems remain, such as: (i) a longer reaction time for ethanolysis than methanolysis that is nevertheless still acceptable (respectively 45 vs. 15 min with rapeseed oil) [85,86], (ii) greater solubility of glycerol in the ethyl than in methyl esters, but that could be minimized either by evaporation of the alcohol or by addition of cold glycerol to the medium [83,84].

Note that in the future, biomethanol (i.e. renewable methanol) could be produced from biomass, either by fermentation or thermal conversion. The last process, being the most promising, has yet to be optimized to become economically viable [6,45].

#### 3.2. Catalytic and non-catalytic conversion processes: from classical to supercritical route via the intermediary heterogeneous method

As mentioned previously (Section 2.2), non-conventional lipid resources (NEVO, WCO, algal lipid) may contain a high-content of FFA and water. Within catalyst-based conversion processes, alkaline catalysis can be used up to an FFA content in the TG stock of

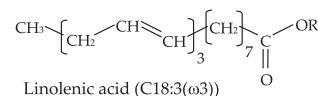
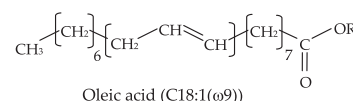
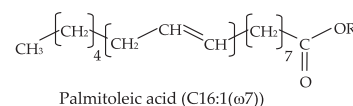
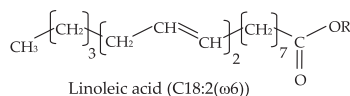
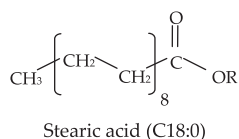
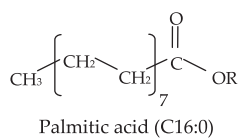


**Fig. 1.** Transesterification reaction of triglycerides. (a) Overall chemical equation illustrated for ethanolysis yielding FAEE and glycerol ( $R_1, R_2, R_3$  are identical or different aliphatic chains with zero to three unsaturated bond(s):  $\text{CH}_3-(\text{CH}_2)_m-(\text{CH}_2-\text{CH}=\text{CH})_n-(\text{CH}_2)_k$  with  $(m+k) = 12, 14, 16, 18$  or  $20$ , and  $n = 0, 1, 2$  or  $3$  (6 for fish oils)). (b) Alcoholysis of triglycerides as a sequence of three consecutive and reversible reactions. Note that in case of supercritical alcoholysis, the use of a catalyst is not necessary [42].

**Table 1**  
Average fatty acid compositions of some vegetable oils and fats [42,77,78].<sup>a</sup>

Vegetable oil	Palmitic acid C16:0	Palmitoleic acid C16:1(ω7)	Stearic acid C18:0	Oleic acid C18:1(ω9)	Linoleic acid C18:2(ω6)	Linolenic acid C18:3(ω3)	Others (C14 <sup>b</sup> or ≥C20 <sup>c</sup> )
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Rapeseed	3.8	0	2.0	62.2	22.0	10.0	0
Safflowerseed	7.3	0	1.9	13.6	77.2	0	0
Sunflowerseed	6.4	0.1	2.9	17.7	72.9	0	0
Linseed	5.1	0.3	2.5	18.9	18.1	55.1	0
Palm	43.4	0.3	4.4	40.5	10.1	0.2	1.1 <sup>b</sup>
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Tallow	29.5	0.1	19.3	44.4	2.9	0.9	2.9 <sup>b</sup>
Jatropha	13.8	0	6.8	41.7	35.6	0.1	2.0 <sup>c</sup>
Neem	17.6	0	19.3	55.5	9.0	0	0
Karanja	5.8	0	5.6	71.3	15.0	0	2.3 <sup>c</sup>

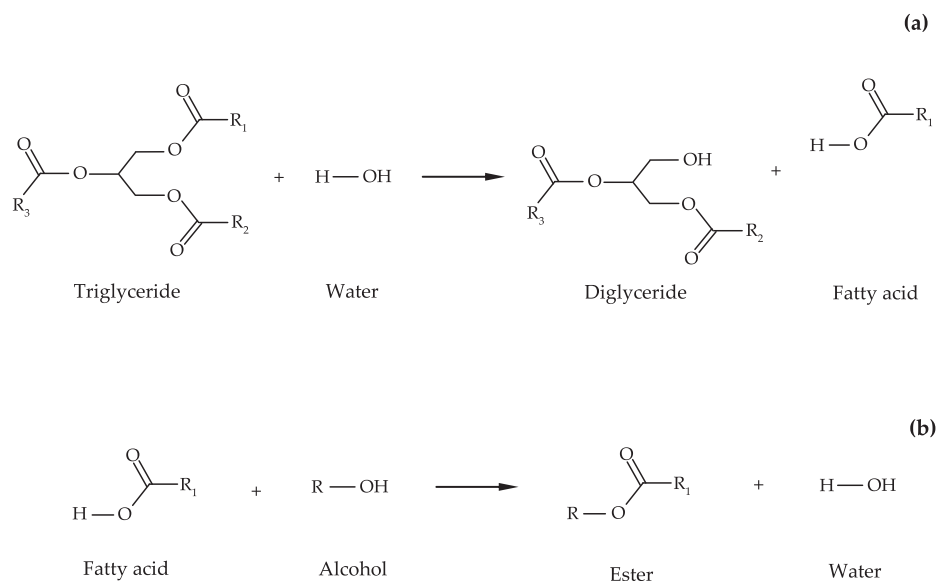
Extended molecular structures<sup>d</sup>



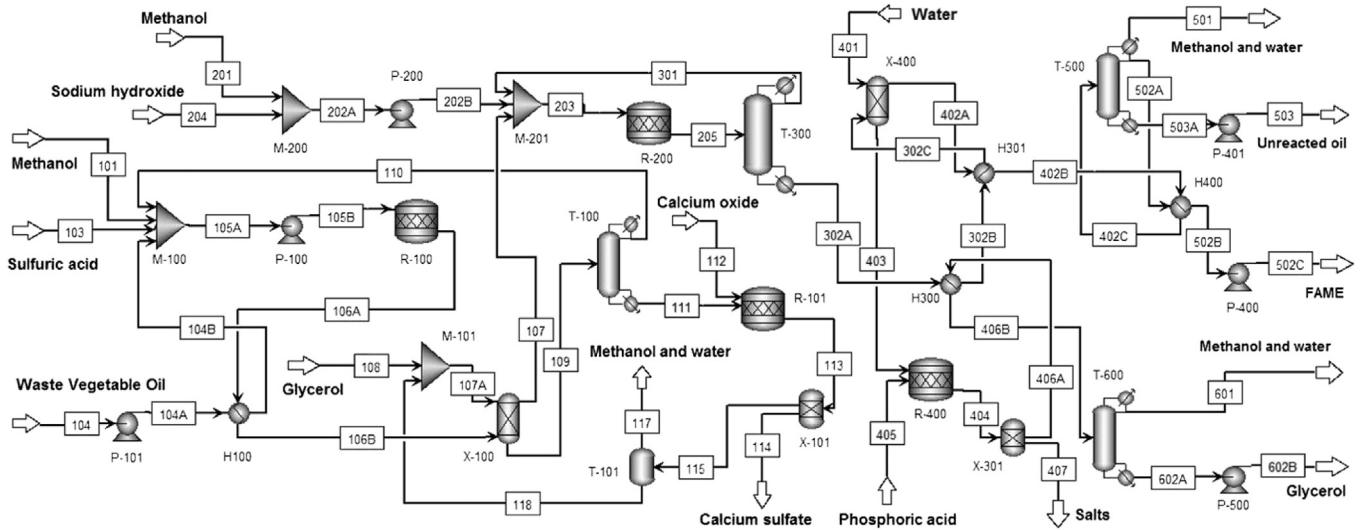
- <sup>a</sup> In Cxx:n(ωy), xx: number of carbon atoms; n: number of double bonds; y: position of the first double bond on the aliphatic main chain, starting from the extremity CH<sub>3</sub>.  
<sup>b</sup> Myristic acid.  
<sup>c</sup> Arachidic acid.  
<sup>d</sup> When R = H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, molecules are respectively FFA, FAME or FAEE.

circa 1 wt% [67]. For TG stocks with a higher FFA content, acidic catalysts must be used [87], unless a supercritical process is adopted. Processes based on homogeneous catalysis (mainly alkali catalysis) are the most widely used for industrial biodiesel

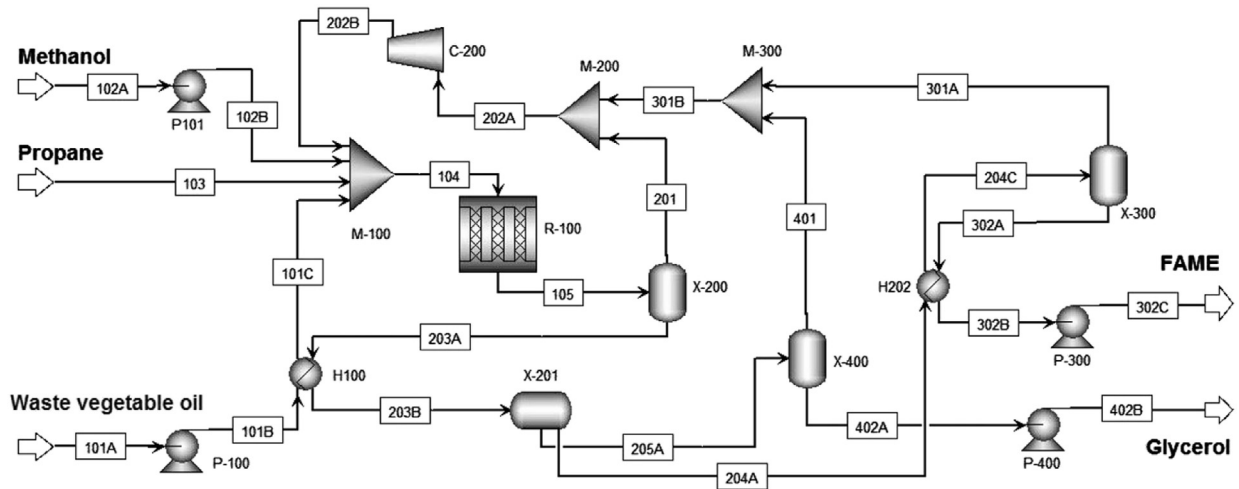
production [88,89]. Other alternatives based on heterogeneous catalysis were proposed in order to avoid catalyst losses and important water consumptions when removing the catalyst from biodiesel by wet-washing [90–92]. Nevertheless, a more critical



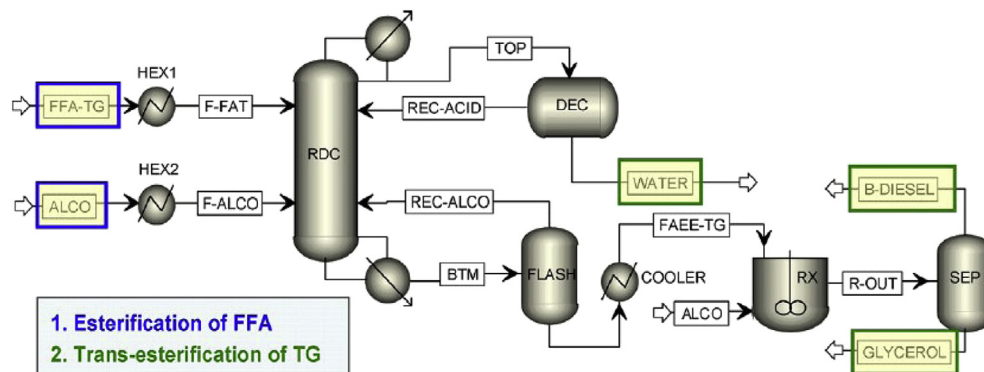
**Fig. 2.** Supplementary reactions to transesterification of triglycerides in case of biodiesel production from non-conventional lipid feedstocks (non-edible vegetable oils, waste cooking oils and animal fats, algal oil). (a) Hydrolysis of triglycerides in FFA. (b) Alkyl esterification of FFA [38].



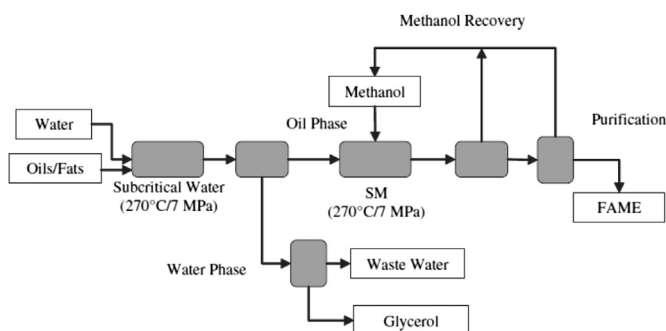
**Fig. 3.** Process flowsheet for the biodiesel production from WCO methanolysis via the classical route (homogeneous alkali-catalysis with FFA homogeneous acid-catalyzed pre-treatment, the whole of the process operating under atmospheric pressure) [95].



**Fig. 4.** Process flowsheet for the biodiesel production from supercritical methanolysis of WCO with addition of cosolvent (propane) [95].



**Fig. 5.** Flowsheet for a two-step atmospheric process (1 – Solid acid catalyst FFA esterification by reactive distillation and 2 – Solid base catalyst TG transesterification) for biodiesel production from high-FFA content lipid stocks. Hydrated bioethanol (96 wt%) is used as alcohol [97].



**Fig. 6.** Flowchart of the two-step (hydrolysis–esterification) process by Saka–Dadan [39]. Subcritical water: TG hydrolysis in FFA (+glycerol); SM: supercritical methanol: methyl esterification of FFA in FAME (+water).

issue than the FFA content in the non-conventional feedstocks is the presence of water which induces the deactivation of the catalyst (except enzymatic and some solid catalysts) when the water content is higher than 0.06 wt% [5,93,94]. As a result, changes or specific technologies are needed in catalytic conversion processes when using lipidic stocks with high-FFA and water contents, water being the most critical factor. Non-catalytic methods like Sc-TG transesterification are not affected by these issues and are thus very promising alternatives.

Although the simulation scheme and the actual configuration of a process are very different, the simulation results are able to represent the complexity of the process. To illustrate the difference in complexity of the biodiesel production pathways by methanolysis of WCO, Fig. 3 shows the simulation process using the traditional approach (basic homogeneous catalysis with a pre-treatment unit of FFA by homogeneous acid catalysis, similar to the Lurgi industrial process at atmospheric pressure [95,96]) and Fig. 4 shows the supercritical process with addition of cosolvent (propane) [95]. No comparative study for ethanolysis was found in the literature. However, an alternative process based on the heterogeneous catalysis in two steps (acid/alkaline) at atmospheric pressure was proposed and simulated for the transesterification of vegetable oils by non-anhydrous ethanol (96 wt%) (Fig. 5). The FFA pretreatment step (esterification, Fig. 2b) is conducted in a catalytic reactive distillation column using a water-tolerant solid acid catalyst (sulfated zirconia) and removing continuously water by distillation. This procedure leads to high yields by shifting the esterification chemical equilibrium while preserving the catalyst activity. The TG-transesterification is then conducted in a catalytic reactor with a solid base catalyst (calcium ethoxide) [97]. It should be noted that this heterogeneous alternative in two reaction stages (esterification/transesterification) is specific for treating feedstocks containing water (in addition of FFA) and is thus different from the conventional heterogeneous method converting quasi-anhydrous feedstocks by transesterification [98,99].

Thus, in view of Figs. 3 and 4, it is clear that the supercritical process involves a reduced number of unit operations, the pre-processing steps of the lipids and the washing of biodiesel to remove the catalyst, not being required in this process. The alternative process of heterogeneous catalysis in two stages (Fig. 5) seems as simple as the supercritical process. However, this process has not been yet the subject of a technical and economic evaluation, or comparative study with the supercritical process. On the basis of comparative knowledge between the conventional heterogeneous catalysis method and the supercritical methanol route, the former method involves lower capital investment and manufacturing costs [98,99]. By contrast, an analysis of comparative life cycle, conducted by the same team of researchers on both traditional and

supercritical processes concluded that the latter has a much lower potential environment impact (PEI) [95].

### 3.3. Key benefits within the drop-in-fuels context

Consistent with previous considerations (Section 3.1 and 3.2), several studies have demonstrated the feasibility and advantages of biodiesel production by supercritical processes when compared with the conventional method [38,39,66,95,100]; in addition of benefits previously mentioned (shorter reaction time and, in particular, absence of catalyst allowing a diversification of resources with significant reduction in terms of equipment and effluents), biodiesel and glycerol are produced with high purity (in principle, 99.8% and 96.4% respectively, as obtained by supercritical methanolysis process simulation [79]). This leads to a biodiesel fulfilling the standards EN-14214 or ASTM-D6751 and a more immediate recovery of glycerol (potential alternatives of valorization discussed in Section 3.4), thereby decreasing biofuel overall cost [101].

Although most of these studies are naturally focused on the methanolysis of edible oils (sunflower oil [85,102,103], palm oil and coconut [104,105] or soybean [106]), the most recent have demonstrated the potential of this new approach with non-edible lipid resources (*J. curcas* [107], *P. pinnata* and *Madhuca longifolia* [56], animal fats [108] and WCO [66,86,109–112]). Studies of supercritical ethanolysis are scarcer [6,113] and relate to various oil-bearing plants (sunflower [85], palm oil, groundnuts, *J. curcas*, *P. pinnata* [114], castor [115], and soybean [112,116–119]).

In addition, the presence of water in the supercritical process (up to 50 wt% when tested in methanolysis [120], and up to 10 wt% in ethanolysis (but certainly a larger amount could be used) [112,121,122]) was proven beneficial for the production of biodiesel, while it induces near zero yields for the conventional method (especially in homogeneous catalysis). The explanation is that the water reacts with the triglycerides by hydrolysis to form the FFA which in turn undergo a faster esterification (Fig. 2b) than the transesterification of triglycerides [120], both in supercritical methanolysis and ethanolysis [85]. In fact, the FFA accelerate the hydrolysis of TG and the FFA esterification (as in an autocatalytic process) [123]. Thus, the presence of FFA in the lipid load does not affect negatively the biodiesel production by supercritical process, but instead plays a positive role. The presence of FFA and water allows an operation at lower temperatures, minimizing the degradation of unsaturated esters [116]. In addition, this major advantage allows the use of non-anhydrous ethanol as alcoholic resource (avoiding the costly final stage of dehydration in the process of production of bioethanol [23,124,125]).

Another significant feature of the triglyceride supercritical ethanolysis which is common to any methods based on TG transesterification (including derived methods like hydrolysis/esterification, Fig. 6 and Section 8.2) is that it takes advantage of the long aliphatic chains available in the TG.

Other biofuel alternatives, such as Fischer–Tropsch (FT) diesel, use an approach that first converts the molecules available in biomass into much smaller molecules (synthesis gas) before rebuilding them by another catalytic process into hydrocarbons with long aliphatic chains. This class of biofuel alternative is thus more complex and energy demanding, with loss of efficiency by entropy generation (exergy destruction) during processing because of chemical bond breaking, even if lignocellulosic biomass is used as feedstock (but to a lower extent with natural gas as feedstock). Another alternative, which is intermediate between biodiesel and FT-diesel, is the hydrodeoxygenation of lipid raw materials that leads to long-chain hydrocarbons, known as “renewable diesel”. Knothe [126] concluded in his review that biodiesel and



“renewable diesel” complement each other rather than compete. This conclusion is in agreement with recently obtained observations according to which the combined production of hydrotreated vegetable oil and biodiesel to be afterward blended with fossil diesel fuel is able to improve significantly the fuel performance and emissions, by increasing the cetane number (from 45 to 65, approximately) and by reducing soot production (by roughly 30%) [127]. Nevertheless, the production process of “renewable diesel” requires the use of a catalyst, which may be somewhat restrictive in terms of the nature of the lipid feedstock (particularly regarding water content). This process is however insufficiently described in the literature for an adequate evaluation. Nevertheless, both “FT-diesel” and “renewable diesel”, commonly named hydrocarbon “drop-in fuels” have important advantages: they meet existing diesel, gasoline, and jet fuel quality specifications (which guarantees total engine compatibility) and are ready to use the existing petroleum infrastructure (which avoids any barrier to fast commercialization of biofuels). Hence, within the drop-in fuel context, the three hydrocarbon-based renewable fuels, i.e. diesel, gasoline, and jet fuel, can be obtained by simply changing the distillation cut during the refinery stage. This yields a compatible renewable Jet fuel bringing an alternative solution to biodiesel which is unsuitable for aviation use and even considered as a contaminant of aviation Jet fuel [21]. Furthermore, FT-diesel fuels (and also renewable diesels) give a viable solution to retaining engine performance and reducing legislative emissions. This is mainly due to the composition of these fuels (paraffinic nature with thus a high cetane number) which improves the combustion process (with a shorter ignition delay reducing hence the pre-mixed combustion stage) and emissions (with a lower NO<sub>x</sub> formation) [43,128].

This discussion reinforces the key idea that flexibility and diversity in the conversion processes are required to face the flexibility and diversity of the feedstocks (depending on the feedstock selected on the most wide possible range, the most suitable conversion process could thus be adopted). This key idea is valid as well regarding emerging countries for which ethyl biodiesel based on agricultural and easy available products with an adequate technology of conversion is a potential alternative to tend toward an energetic autonomy. Hence, flexibility and diversity of the feedstocks and conversion processes may help alternative fuels to meet security of supply and sustainability.

### 3.4. Disadvantages and potential solutions

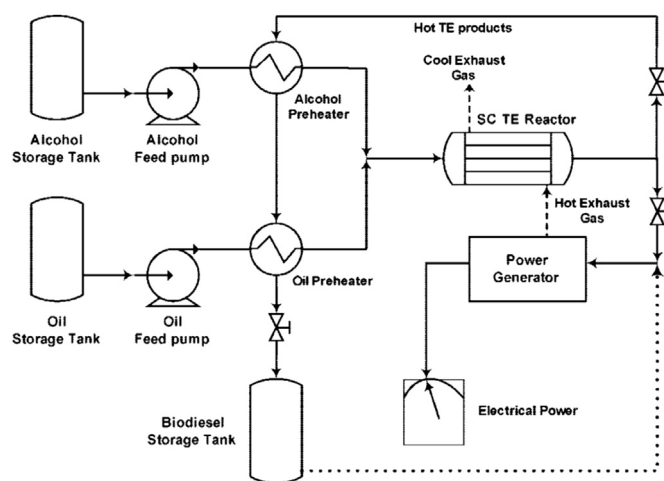
All these studies have concluded that the only major drawback of the supercritical process is its energy demand resulting of tougher operational conditions than the conventional process. In particular, molar ratios of alcohol/oil of about 12, 24 or even 42, temperatures between 473 and 673 K and pressures of 10–20 MPa are most often applied.

Various solutions have been proposed in the literature to reduce the severity of these operating conditions (temperature, pressure, molar alcohol/oil ratio), four of which are described below.

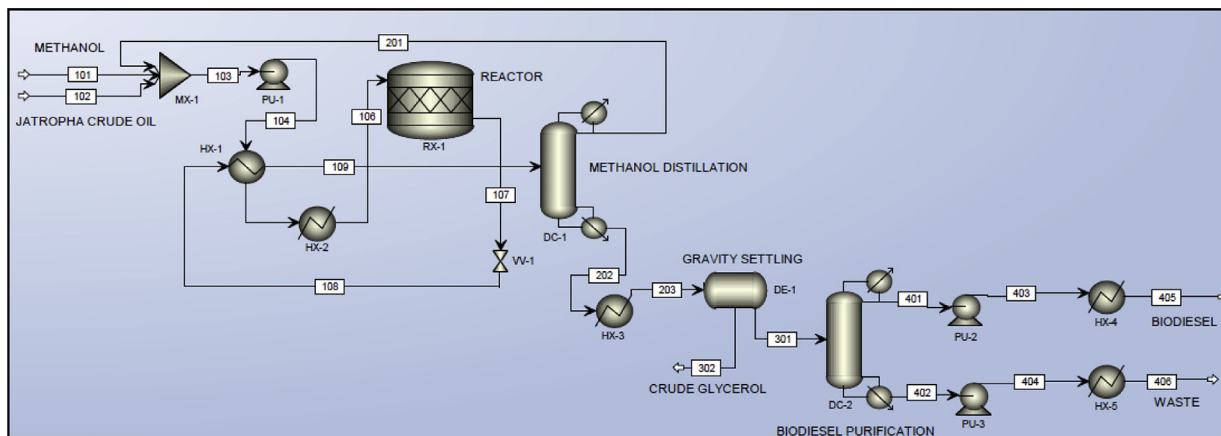
- The first uses the positive effect of water and FFA on the conversion of TG by supercritical processes [120,123], which is then carried out in two steps hydrolysis/esterification (Saka–Dadan process, Fig. 6 [39]). The first step is the hydrolysis of TG in FFA (+glycerol miscible in water); the second step is the esterification of the FFA (Fig. 2). The performance of this process, using supercritical methanol, is best when the FFA content in the lipid load is high and the alcohol/oil ratio is close to 1 (stoichiometric) [123]. An alternative, based on process simulation and proposed to improve the performance of Saka–Dadan process, is to

replace the supercritical FFA esterification reactor followed by purification unit by a reactive distillation (without catalyst) in supercritical methanol. However, the feasibility of this alternative at industrial scale remains questionable [129].

- The second proposed solution is the addition of a cosolvent [38] (propane [86,95,130], hexane [131], heptane [132], or CO<sub>2</sub> [117–119,133]). The inert cosolvent enhances oil-alcohol miscibility and solubility [134], thus reducing the viscosity of the reactive mixture [135], and limits the fatty acid ester thermal decomposition [134]. The cosolvent, however, may also slow down the transesterification rate. Hence, the cosolvent must be introduced in such concentration to adjust the phase behavior of the reactive mixture for the transesterification to take place under favorable conditions, wherein the fatty acid esters yield can be tuned effectively by pressure and temperature [134].
- A third solution to further improve the energy performance of supercritical processes is the integration of a network of heat exchangers [136] or the integration of a cogeneration unit biodiesel–heat–power (Fig. 7). Based on simulations, some authors estimated that the second approach integrating a biodiesel–heat–power cogeneration unit could be up to two times less expensive than the conventional method (for a production capacity of 56,775 L/day, cost of biodiesel: \$0.07/L via the proposed method against \$0.13/L via the conventional catalytic process [134,137]). These estimates were obtained in the case of the methanolysis of soybean oil. However, lower costs are expected using WCO and bioethanol. In addition to the biodiesel–heat–power cogeneration, other factors contributed to the success of this alternative: a molar alcohol/oil needed for the transesterification of 3/1 (stoichiometric) avoiding the costs required to recycle the excess alcohol, and operating below the usual pressures (10–20 MPa) but at high temperatures (673 K). Such operating conditions have led to a 100% oil conversion in FAME, but also to the *in situ* conversion of glycerol into shorter ethers. The resulting mixture is no longer compliant with EN-14214 or ASTM D6751 and cannot thus be considered as biodiesel. It constitutes nevertheless an alternative biofuel with superior combustion performance due to the presence of ethers [138–140]. Other studies addressing the supercritical



**Fig. 7.** Flow diagram for supercritical transesterification of vegetable oils (soybean, sunflower) to biodiesel with integrated cogeneration biodiesel–heat–power [134,137]. The principle behind cogeneration «biodiesel–heat–power» is to recycle part of the produced biodiesel to the power generator which in turn delivers: (1) the electrical power to the pumps and compressors for insuring the pressure rise of the process fluids; (2) the hot exhaust gas for heating the supercritical (SC) transesterification (TE) reactor.



**Fig. 8.** Process flowsheet for biodiesel production from *Jatropha curcas* supercritical methanolysis [107]. Simulation carried out with Aspen HYSYS® & Aspen Plus® release 12.1. Operating conditions: reactor RX-1 (623 K, 20 MPa), distillation columns DC-1 (~0.1013 MPa with 7 theoretical stages), DC-2 (~0.05 MPa, 13 theoretical stages), decanter DE-1 (~0.1013 MPa).

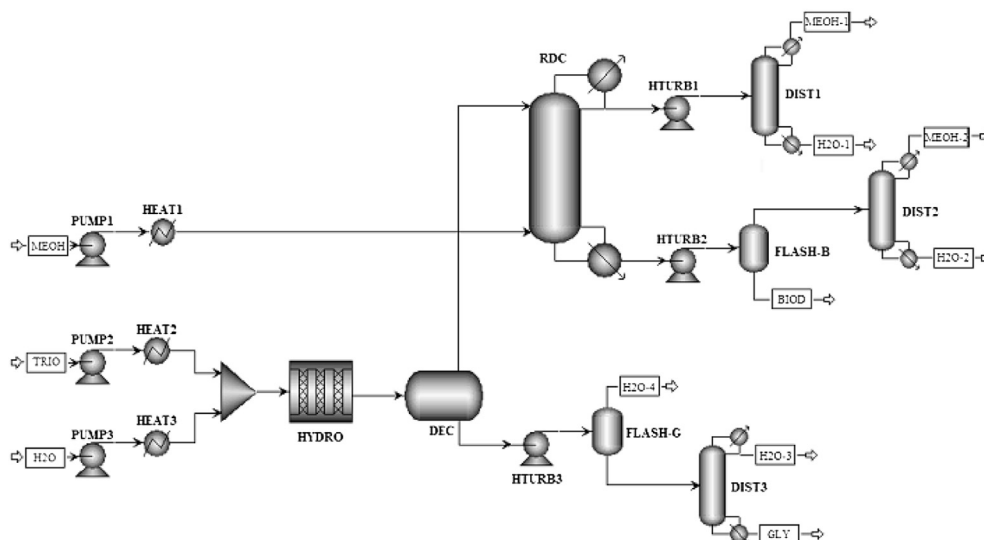
conversion of TG confirm the importance for the PEI of a reduction in the alcohol/oil ratio (at least to 9/1), even increasing the reaction temperature (673 K), for a total conversion of the oil in esters with *in situ* glycerol etherification [100,141].

In addition, for the cogeneration alternative, agricultural waste materials like rice or *Jatropha* seed husks could be used as fuel to replace the biodiesel [54,58,142,143]. Moreover, the recovered ashes are natural adsorbents that have shown an excellent performance in purifying biodiesel by removing catalyst, glycerol, glycerides and residual water [113,144,145]. Such a solution, integrating the bio-refinery concept, would help reducing environmental impacts.

- Regarding the fourth solution, for supercritical processes aimed at the production of a biodiesel fulfilling the standards (i.e. not containing ethers resulting from *in situ* decomposition of glycerol), an additional alternative to improve the energy and environmental performance of the process (and therefore its LCA) is to integrate the valorization of glycerol coproduced in

the process. Among the various ways of upgrading crude glycerol proposed in the literature [32,54,101,146–151] a guided selection, depending on the nature of the resources and the conversion process used, suggests as options:

- ◆ Electrical power and hydrogen production from glycerol reforming using supercritical water via a system energetically self-sustained [152,153],
- ◆ Catalytic valorization of glycerol to hydrogen and syngas [148],
- ◆ Production of biohydrogen and bioethanol by bioconversion of glycerol with microbial mixed culture [154],
- ◆ Catalytic etherification of glycerol at low temperature (343 K) in oxygenated fuel additive (glycerol alkyl-ether) suitable for diesel and biodiesel with better combustion and emission performances [155],
- ◆ Neutralization of high-FFA content oils via the crude glycerol obtained as byproduct of alkali-catalyzed transesterification [54],
- ◆ Production of docosahexaenoic acid (DHA) and palmitic acid through algal fermentation on crude glycerol as carbon source [156].



**Fig. 9.** Two-step biodiesel production process (subcritical hydrolysis/supercritical esterification with methanol) by non-catalytic reactive distillation [129]. TRIO: surrogate molecule of vegetable oils. Simulation carried out with AspenOne™.

The last alternative would be recommended for lipid feedstock derived from microalgae whilst all others are suitable for any lipid resource adopted.

#### 4. Analysis, simulation and optimization of the supercritical process – basic theoretical knowledge to expand and develop

One of the advantages of process simulation is that it allows to establish a link between raw materials and targeted products, taking into account all the input/output of utilities in terms of matter and energy. Being a virtual process, after a first design draft, the operation can be simulated and optimized to meet the requirements imposed (e.g. minimization of equipment costs, input/output of materials, energy and waste streams, to achieve an “eco-design”, and maximize the yield of biodiesel). The ideal process meeting the requirements is obtained after this optimization step. The best approach to validate the estimates made by the process simulator is to directly compare these results with experimental data gathered from unit operations scalable to an industrial scale. The reliability of the estimates obtained from a process simulator is dependent on the performance of the theoretical models used to describe the thermodynamics, kinetics, and transport phenomena involved in the various unit operations of the process [25,97]. These phenomena are specific for the mixtures and operation conditions used.

In the literature, studies have been reported for the simulation of a supercritical biodiesel production process for the couple “WCO or NEVO & methanol” with [86,95] (Fig. 4) or without the addition of a cosolvent (propane) [66,98–100,107,157] (Fig. 8). A recent study also suggests an improvement to the Saka–Dadan process, still addressing the methanolysis [129] (Fig. 9). The supercritical ethanolysis was up to present only investigated considering edible vegetable oils (palm oil) [141].

Although most authors have used a process simulator widely recognized as the “standard” for the chemical industry due to its depth and breadth (Aspen HYSYS® and Aspen Plus®, from Aspen Technology, Inc. Massachusetts), limitations are nevertheless identifiable on the kinetic and thermodynamic models used to describe the production of methyl biodiesel as discussed below (Sections 4.1 and 4.2). These limitations are even more pronounced in the context of processes under development such as the supercritical production of ethyl biodiesel in the presence of CO<sub>2</sub>.

##### 4.1. Theoretical basis for the description of kinetic phenomena

Kinetic models were developed following two main approaches, one at molecular scale (so called molecular approach), and the other at reactor scale (so called macroscopic approach).

###### 4.1.1. Molecular approach

The molecular kinetic approach is based on the detailed transesterification reaction mechanism and the rate laws for each of the eight basic steps involved (Fig. 1, reaction equations must be considered in the forward and reverse directions). Established on the basis of the kinetic data linking the composition of the various molecular species present in the reaction medium as a function of time, temperature, pressure and concentration, the resulting molecular models are specific to the molecules and operating conditions. Thus, to represent the lipids, the molecular approach requires the definition of surrogate molecules with the TG being typically mimicked by triolein, leading to diolein and monoolein as intermediate glycerides and methyl oleate as final biodiesel. The free fatty acids present are represented by oleic acid.

Although this detailed approach has been adopted for some transesterification studies using homogeneous catalysis at

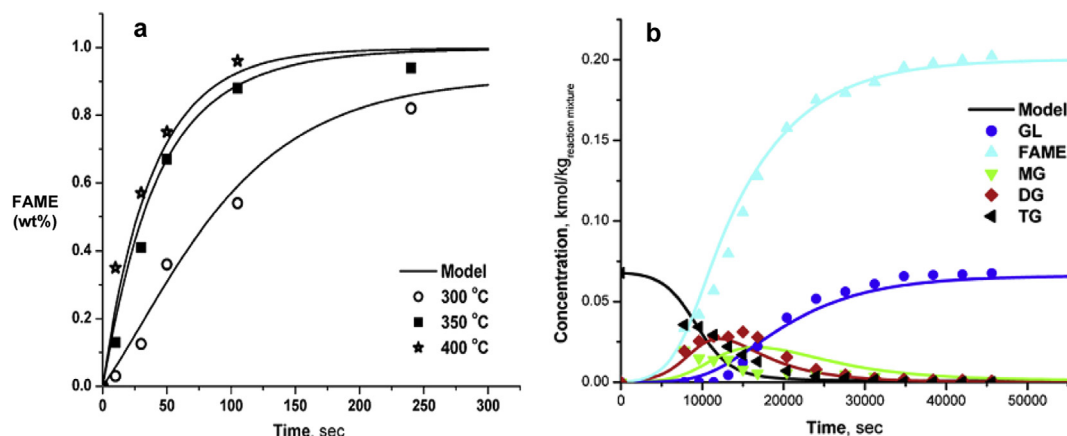
atmospheric pressure [158,159], a simplified approach has been generally used for supercritical processes. Considering that all the TG, DG, and MG molecules (and the FFA possibly present) represent the unconverted oil, and assimilating it to a pseudo-component, only the overall transesterification reaction was considered (Fig. 1a replacing TG by the unconverted pseudo-component). In addition, given the high molar ratio alcohol/oil (ranging from 12 to 42), the reverse reaction was rightly ignored and the alcohol concentration considered constant. The rate constant of the reaction, assumed of pseudo-first order, was then determined by fitting to the experimental data of the oil concentration as function of time, and the activation energy of the reaction from the rate constant values at various temperatures using the Arrhenius law. In process simulation the researchers have no other choice than to describe the phase equilibria considering the various surrogate molecules of TG, DG and MG and to adopt global kinetic laws established for different oils, selecting the closest to their case study. Kinetic studies involving this simplified molecular approach have been used mainly for edible oils undergoing a methanolysis (rapeseed oil [160], soybean [161], peanut [162], sunflower [163]) and supercritical methanolysis or ethanolysis (palm [114], sunflower oil [164], castor and linseed [165]). Kinetic studies for non-edible oils in supercritical conditions are scarce. Only the methanolysis and ethanolysis of *Jatropha* oil has been reported [114].

The results of these studies confirm that the apparent activation energies of supercritical alcoholysis are highly dependent on the nature of the oil (in addition to the nature of the alcohol). Consequently, the molecular approaches, both the detailed using surrogate molecules or simplified considering the oil as a pseudo-component, are biased. However, only such a kinetic approach can be combined in principle with theoretical models to be able to describe the phase equilibria and transport phenomena at the molecular scale, and thus to capture specifically the complexity of the supercritical alcoholysis of lipids. The actual limitation lies in the numerical resolution of the model equations, leading inevitably to simplifying assumptions (e.g. the conversion of TG as the only variable). The model developed by Glišić and Orlovic [163] serves to illustrate this point (Fig. 10). As shown by the authors for the supercritical methanolysis of sunflower oil, the model provides a very good representation of the experimental data accurately describing the changes over time of the various species present in the reaction mixture.

###### 4.1.2. Macroscopic approach

The macroscopic kinetic approach is based on the knowledge of conversion of lipidic resource (TG) from design of experiments, together with the reactor design equations giving reaction rate (rate of disappearance of TG) as function of conversion [166].

Design of experiments (DOE) derive from a statistical methodology that defines the minimum number of experiments required to reliably establish the relationship between conversion and the observable variables that play a key role in the reaction unit (temperature, pressure, alcohol/oil and alcohol/cosolvent molar ratios, time...). Various methods can be used to generate the DOE (e.g. full factorial or central composite, Doehlert design, D-optimal design) usually in conjunction with the response surface methodology (RSM) to check the reliability of the method and identify the optimal values of the key reaction unit variables leading to the maximum resource conversion. The resulting macroscopic models are thus specific to both the resources (oil, alcohol, cosolvent) and the conversion process. Given the compositional complexity of the lipid resources to be converted (Fig. 1 and Table 1), many studies focused on the biodiesel production reaction unit have adopted this approach within the conventional method to convert edible oils by methanolysis [167–169] or ethanolysis [170,171], or even WCO, animal fats and NEVO by methanolysis [172–175]. The studies



**Fig. 10.** Modeling [163] and experimental data [160,163] of sunflower oil supercritical methanolysis (Methanol/oil molar ratio = 42/1). (a) Methyl ester content (wt%) from Kusdiana and Saka (573–673 K, 20 MPa) [160]; (b) concentrations in species of the reaction mixture from Glišić and Orlovic (483 K, 4.5 MPa) [163].

related to the supercritical process via the macroscopic approach (both by methanolysis and ethanolysis) concern mainly edible oils (palm [176,177] or rapeseed [178]), and occasionally NEVO [35,179,180].

Hence via the DOE, an expression of the maximum conversion as a function of time (and possibly temperature) can be derived by fixing the other reactor key variables to the optimal values determined via RSM. This expression can then be combined with the reactor design equations in order to acquire the rate of reaction (rate of TG disappearance) according to the reverse procedure of that commonly adopted for designing isothermal reactors (with a given rate law and a conversion specified as objective) [166].

#### 4.1.3. Complementarity between molecular and macroscopic approaches and suggestions for future developments

It is essential to understand that the two approaches are worth considering (or developed) in synergy because of their complementarity. Indeed, in the molecular approach, the gains obtained by using the size of molecules to describe their kinetic behavior is offset by the need to use surrogate lipid molecules or to adopt the rate constant of alcoholysis of a similar oil (i.e. with a similar fatty acid composition). Concerning the macroscopic approach, the advantages from considering the actual lipids is offset by the globalization of their kinetic behavior estimated from the input–output of the reactor. Accordingly, a multi-scale kinetic modeling (macroscopic and molecular) able to describe the supercritical ethanolysis of lipids or their surrogate molecules with addition of CO<sub>2</sub> as cosolvent would be the best compromise, and future developments would benefit from this approach.

A formal description of the procedure combining the multi-scale kinetic modeling (macroscopic and molecular) can be given by:

Thus, the rate of disappearance of TG (rate of reaction) determined via macroscopic modeling can be used for estimating the parameters of a postulated rate law according to molecular modeling. Moreover, a thermodynamic model will be used simultaneously to inform on the phase equilibria behavior of the reaction medium in order to develop and apply the kinetic models under relevant conditions.

#### 4.2. Theoretical basis for the description of thermodynamic phenomena

Only thermodynamic models using an equation of state (EOS), relating temperature, pressure, volume conditions and mixture composition, are acceptable to realistically represent the phase

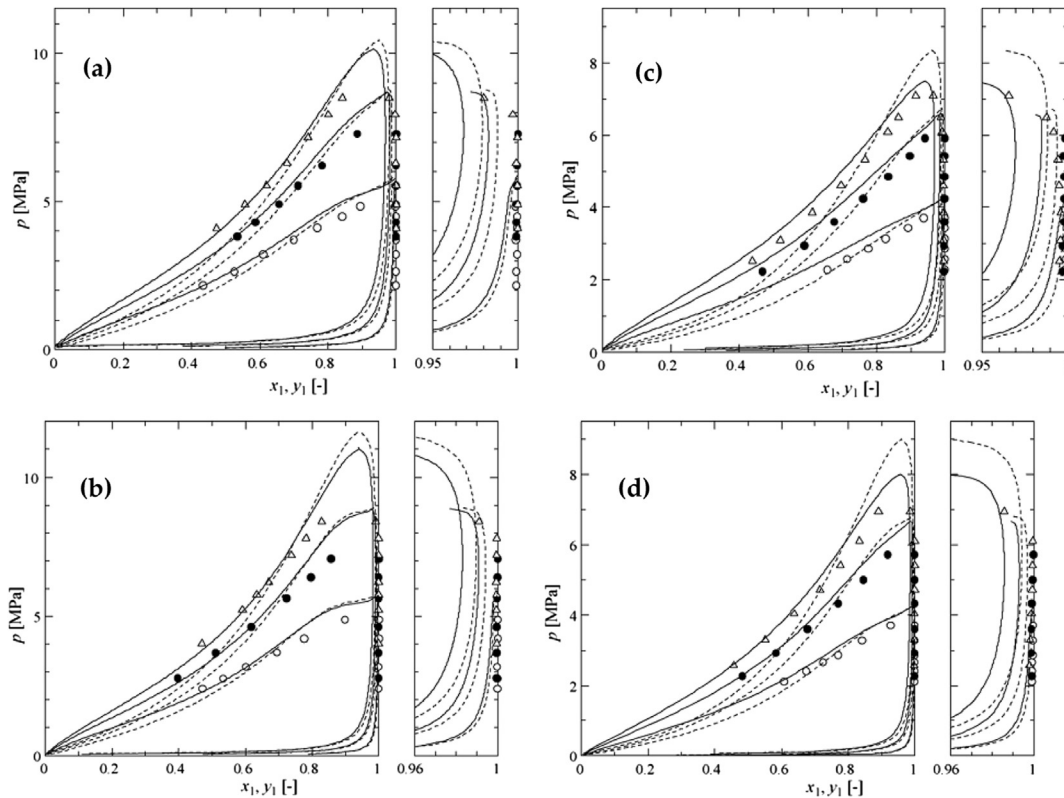
equilibria at high pressure and/or near the critical point of at least one of the constituents of the mixture (i.e. CO<sub>2</sub>, ethanol or methanol). These phase equilibria found at the various process units (Fig. 8) correspond to:

- Supercritical monophasic (ScE), vapor–liquid (VLE) or vapor–liquid–liquid (VLE) under high pressure (HP) and high temperature (HT) in RX-1;
- Vapor–liquid–liquid (VLE) under medium to low pressure (MP & LP) and medium to high temperature (MT & HT) in DC-1;
- Liquid–liquid (LLE) at LP in DE-1;
- VLE under MT & LT-LP in DC-2.

#### 4.2.1. Relevant thermodynamic approaches: molecular vs. group contribution, and association EOS

Two thermodynamic approaches are possible: the molecular approach (leading to molecular models) and the approach based on the concept of group contributions (leading to GC models). In GC models, a mixture is considered as the set of functional groups defining the structure of its components (methyl groups, allyl, ethyl ester, carboxylic ...) In contrast, in molecular models, a mixture is viewed as a set of molecules. If based upon a large enough dataset of phase equilibria of binary mixtures, the GC model is fully predictive and can be generalized to any mixture involving the structural groups defined. However, the GC model is less accurate than the molecular model. The latter is able to capture more particular structural aspects, but it is also specific to the binary data used to establish the model and thus, cannot be applied to a multicomponent mixture containing a large number of constituents (unless a great deal of time and money is spent to generate all the binary subsystems required). Also, since the GC models are generalizable they are the basis for process simulation, but their reliability needs to be established. Molecular models can help to check the GC model reliability by comparing their respective performance on experimental data (equilibrium measurements or data on process operating points). In addition, the more accurate molecular models may be used as data generator to inform, and thus extend, the GC models. Reciprocally, the GC models may also be used as data generator, admittedly with inferior accuracy compared to molecular models, but with the advantage of extending them to multicomponent systems for which some binary subsystem parameters are missing due to lack of experimental data. Thus, GC and molecular thermodynamic models are complementary and should be considered and developed in synergy.

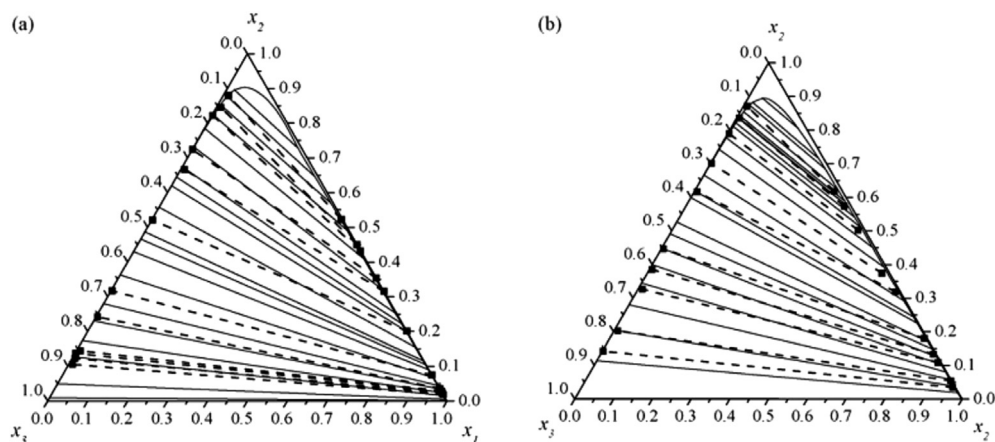




**Fig. 11.** Vapor–liquid equilibria of methanol/ethanol + methyl/ethyl myristate/laurate binary systems: (a) methanol(1) + methyl laurate(2), (b) methanol(1) + methyl myristate(2), (c) ethanol + ethyl laurate(2), (d) ethanol(1) + ethyl myristate(2). Experimental data: [188] for (a) and (b), [190] for (c) and (d), where (○) 493 K, (●) 523 K, (△) 543 K. Prediction results: (---) SRK/WS/UNIFAC, (—) SRK/WS/COSMO-SAC [195].

Furthermore, the chemical structure of the molecules involved in the production of biodiesel induces molecular associations between molecules of the same or different type due to the glycerol, alcohol and water present in the system. These associations may be mitigated by the main aliphatic chain length of the glycerides and methyl or ethyl esters, but they must be nevertheless taken into account by the thermodynamic model. Unfortunately, the simulation studies on the process of biodiesel production by supercritical alcoholysis cited above did not use models with EOS taking into account the molecular associations, simply because such models, applicable to the mixtures under study, are not yet available in process simulators.

However, recent work combining experimental and theoretical aspects related to the supercritical alcoholysis of vegetable oils and surrogate molecules (with detailed phase diagrams) have appeared in the literature. These measures cover various phase equilibria (LP-LLE [181–186], HP-VLE [187–190], LP-VLE [191–194] and MP-VLE [182]) over a wide range of temperature and pressure, and systems related with methanolysis (involving FAME or methanol, besides TG and glycerol) [181,182,186,188,189,194] and ethanolysis (involving FAEE or ethanol, besides the TG and glycerol) [183–187,190–194]. A more detailed description of these data is provided below (Section 6.2). The theoretical work, to reproduce and predict these phase equilibria, led to the development of two GC–



**Fig. 12.** Comparison between GCA–EOS predicted (solid lines) and experimental [182] (dashed lines) tie lines of the ternary system methyl oleate(1) + methanol(2) + glycerol(3) at (a) 313 K, (b) 333 K [199].



EOS models able to account associations: SRK–WS–COSMO–SAC [195] and GCA–EOS [182,196–200]. More recently, the CPA–EOS model, based on the molecular approach combined with an association EOS has also been proposed as a complement [201–205]. Figs. 11–13 give an overview of the performance of these models in terms of predicting phase equilibria of various mixtures involved in the production of supercritical methyl and ethyl biodiesel.

#### 4.2.2. Suggestions for future refinements of thermodynamic models

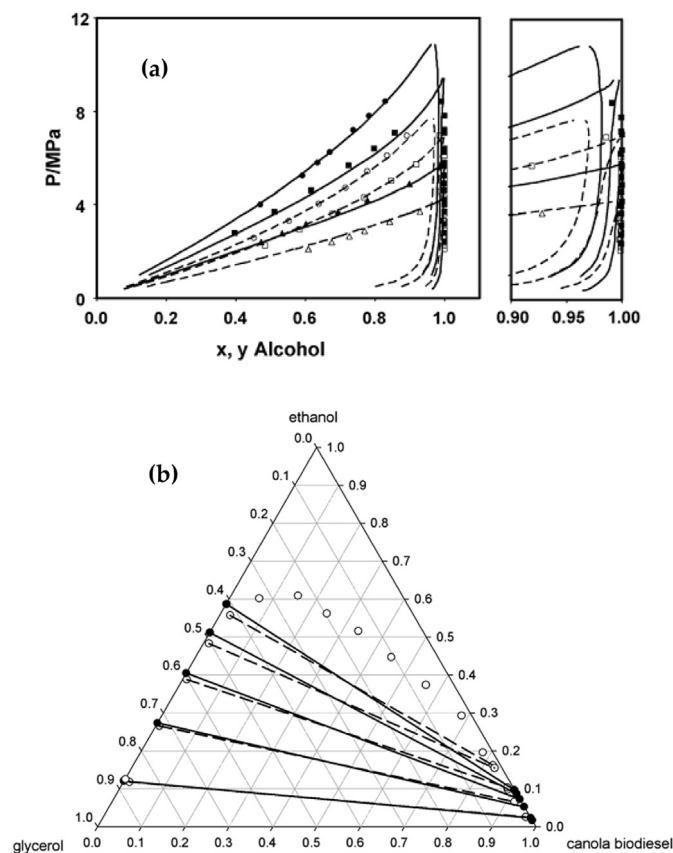
The works mentioned above [181–205] need to be extended to the “biodiesel produced by supercritical ethanolysis with added  $\text{CO}_2$ ” for reliable simulations of the production process. For binary and multicomponent systems involved in the industrial process, additional experimental data (ScFE, VLLE, LLE and VLE) should be generated for the adaptation or development of new models. The systems to be studied would contain FFA and water, in addition to basic components, such as ethanol, TG,  $\text{CO}_2$ , glycerol and FAEE. Besides the extension of SRK–WS–COSMO–SAC [195], GCA–EOS [182,196–199], or CPA–EOS [201–205] models, it would be interesting to adapt the model PPR78 [206], combining GC and EOS, by the introduction of an association term in this model.

The model PPR78 is already implemented in a commercial process simulator (ProII, from Invensys Systems, UK). Moreover this model has proven its quality in the prediction of phase equilibria and thermal properties required to estimate the energy balance (excess enthalpy and heat capacity) for multicomponent systems

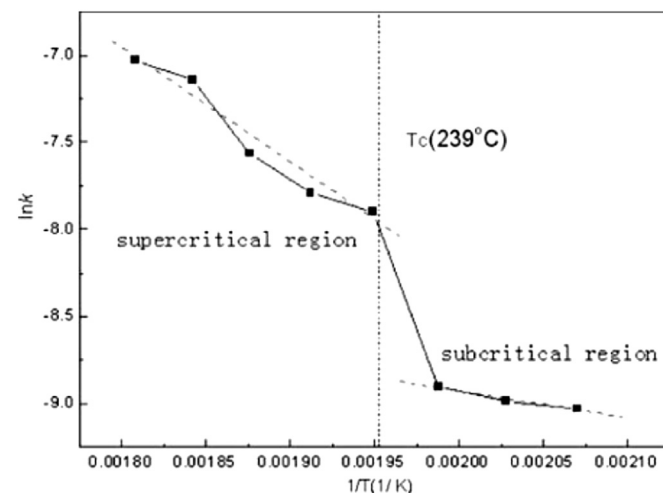
involving hydrocarbons, mercaptans, the  $\text{CO}_2$  and other gases ( $\text{H}_2\text{S}$ ,  $\text{H}_2$  and  $\text{N}_2$ ) [206]. The association term introduced in CPA–EOS could be replicated and adapted to PPR78 because the two models have physical parts based on the same type of EOS. Thus, such a model, after introducing an association term would be useful not only for the simulation of the entire production process, but also in the formulation of “biodiesel-petrodiesel” mixtures, or even at description of the physical phenomena of combustion in diesel engines.

### 5. Synergies between kinetics and thermodynamics in the supercritical transesterification of lipids

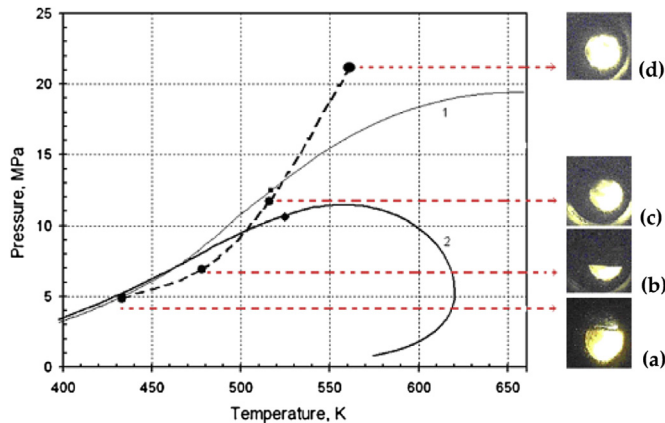
It is essential to have an accurate monitoring of the transition between the subcritical and supercritical regions of the reaction mixture because during this transition, like most physico-chemical properties of fluids, the kinetic constant of the alcoholysis undergoes a sudden change [207,208]. Fig. 14 illustrates this phenomenon, justifying the increases observed in the yields of esters of 10–20% (depending on the oils and alcohol used) when moving from subcritical to supercritical region [209,210], with the further advantage of shorter reaction times [116,210]. Additional interpretation of this phenomenon is obtained through the phase envelope of the reaction mixture at the beginning and end of the reaction, and the transesterification PT reaction path during the heating phase [179] (Fig. 15). As can be seen, during the pressure and temperature rise to achieve the supercritical transesterification conditions, the reaction mixture changes from a two-phase state (subcritical region) to monophasic (supercritical) without limitations to the mass transfer, which accelerates the reaction (in addition to the specific chemical properties that the alcohol develops at the supercritical state). The transition between the subcritical–supercritical regions occurs over a few tenths of Kelvin and a few thousandths of bar, it is thus essential that the thermodynamic models are very specific to describe the exact conditions of the phase transition. The better the critical point of the reaction mixture can be accurately described for a good representation of the phase envelope (for each mixture formed during the reaction progress), the better and more reliably the optimal reaction path can be predicted (leading to maximum reactivity and mass transfer, with minimum energy requirements). Regarding the highly complex systems involved in biodiesel production, particularly when



**Fig. 13.** Performance of CPA–EOS regarding VLE and LLE for systems involved in biodiesel production [201,202]. (a) VLE for methanol + methyl myristate (full symbols) and ethanol + ethyl myristate (empty symbols) systems (triangles, 493 K; squares, 543 K); CPA–EOS estimations (—, methanol based systems; ---, ethanol based systems) [201]. (b) LLE for the systems canola oil ethyl biodiesel + ethanol + glycerol at 303.15 K; experimental (empty symbols and dashed line) and CPA–EOS estimations (full symbols and solid line) [202].



**Fig. 14.** The first order reaction rate constant of soybean oil methanolysis in Arrhenius plot and effect of the phase equilibrium of soybean oil and methanol on the kinetics of methanolysis (Methanol to oil molar ratio = 42/1,  $P = 28$  MPa) [161].



**Fig. 15.** Kinetic and thermodynamic monitoring of soybean oil supercritical methanolysis during the heating process (global density in the reactor:  $0.645 \text{ g/cm}^3$ , methanol/oil molar ratio: 65.87, 24.11 wt% propane) [198]. Legend: line 1 – phase envelope of the TG used as soybean oil surrogate + methanol + propane (cosolvent) representing the reaction mixture at the start of the methanolysis, line 2 – phase envelope of the FAME + methanol + glycerol + propane (cosolvent) representing the reaction mixture at the end of the methanolysis (100% oil conversion), dashed line – PT history of the methanolysis. The filled diamond symbol denotes the critical point of the reaction mixture involved in line 2. Lines 1 and 2 are predicted by GCA–EOS model. During the heating process, the reaction mixture is successively biphasic (a–c), and then monophasic (d), (c) showing the transition to liquid–supercritical fluid equilibria (opalescence of the upper phase), and (d) representing the mixture at the end of the reaction.

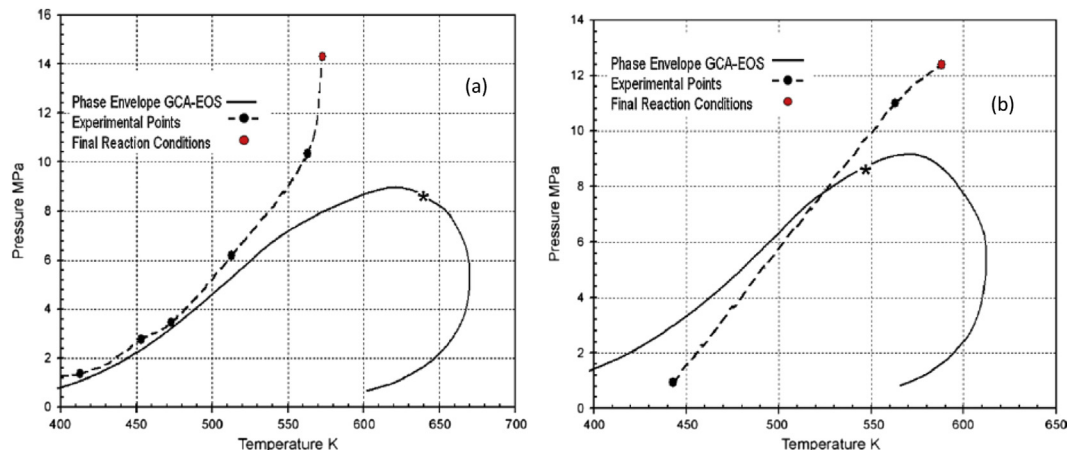
dealing with resources containing water and FFA, this accurate description of the critical region by the thermodynamic models cannot be reached without applying a crossover to an association EOS [211].

Another pertinent route for selecting *a priori* the phase equilibria condition of the reacting system is to consider the global density defined as the total mass charged into the reactor divided by the reactor volume [198,207]. Indeed, in addition to be composition dependent, density is a very sensitive variable with respect to pressure and temperature near critical region and there is a clear relation between global density, phase behavior and reaction pressure as highlighted by Hegel et al. [198]. This phenomenon is illustrated by Fig. 16 showing the trajectory of transesterification experiments carried out at different global densities ( $0.8$  and  $0.5 \text{ g/cm}^3$ ) [207]. In the VL region, depending on the global density of the

reacting mixture and on the location of its critical point on the phase envelope, either the liquid or the vapor phase increases up to a point at which the whole mixture becomes homogeneous. However as it can be observed, at high global densities the reaction takes place in the liquid phase where the pressure increases drastically with temperature (Fig. 16a). By contrast, such steep variations in pressure vs. temperature do not occur at lower density, making the reaction to occur in gas phase (supercritical region) easier to be controlled and in a lower pressure range (Fig. 16b). Note that comparison of Figs. 15 and 16b shows graphically the impact of the addition of a cosolvent (propane) to the supercritical transesterification. As can be seen, an increase in the cosolvent content at constant alcohol/oil molar ratio decreases the reaction mixture critical temperature, enabling to operate in supercritical region under milder thermal conditions. A similar effect occurs when increasing the alcohol/oil molar ratio (at constant cosolvent content), with an additional thermo-chemical effect due to the shift of the chemical equilibrium toward the esters by addition of excess reactant.

Global density also helps to understand the effect of heterogeneous phase conditions on biodiesel production. Indeed, high conversion has been observed even by operating in the two-phase VL region [198], probably because the operating density of the reacting mixture corresponds to a value leading to a sufficient amount of vapor phase. The authors [198] explained that in such circumstances the oil transesterification probably occurs mainly in the light supercritical phase, where the glycerides are partially soluble and the alcohol concentration is high, with species mostly under non-associated form [102].

Furthermore, since density of a reacting mixture determines the residence time in the reactor and given its high sensitivity around the critical region, accurate determination of this variable (either via experiments or via reliable thermodynamic models) is important for the design of continuous supercritical reactors and the determination of kinetic parameters. Assuming ideal solution behavior for density calculation, which is usually done, may lead to important deviations in the residence time and thus in the kinetic rate [212]. As illustrated by Fig. 17, relative errors in the estimation of the residence time assuming ideal solution may range from 20 to 13% depending on the residence time value (12 and 45 min respectively), and may increase up to 50% with temperature (from 593 to 618 K). These errors lead then to overestimate the kinetic constant with relative errors increasing from 5 to 18% with increase in temperature from 593 to 618 K [212].



**Fig. 16.** Product phase-envelope (full lines) and reaction trajectories (dotted lines) for different global density in the supercritical methanolysis of refined soybean oil. (a)  $0.8051 \text{ g/cm}^3$  and (b)  $0.5130 \text{ g/cm}^3$  (methanol/oil molar ratio: 65.88, 4.68 wt% propane) Legend: final conditions of the reaction system (●); phase envelopes predicted by GCA–EOS of the final reaction system [methanol + propane + soybean oil FAME + glycerol] for a 100% oil conversion; critical point of the final reaction system (★) [207].

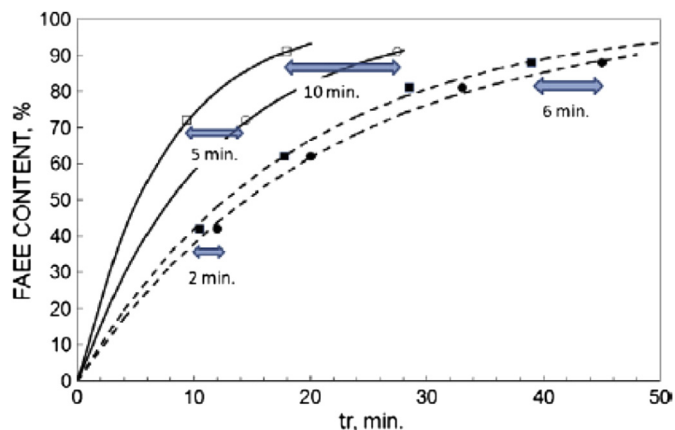


Fig. 17. Continuous supercritical ethanolsis of sunflower oil – experimental reaction conversion (product FAEE content) at 593 K (dashed lines) at 618 K (solid lines) vs. residence time. Legends: ■ and □: residence time assuming ideal solutions; ● and ○: residence time estimated on the basis of experimental PVT data [212].

With such representations it is thus possible to have a better understanding of the influence of the thermodynamic behavior of the reaction mixture under the reaction progress in order to predict, after the development of a proper kinetic and thermodynamic model, the optimal operating conditions of the reactor resulting in a maximum yield of biodiesel and minimum energy demand [113,179,208,213]. It should be, however, noted that the phase diagrams describing the thermodynamic behavior of the mixtures considered, do not account for the possible formation of thermal decomposition products under the effect of a too high reaction temperature [113]. These considerations show that the two aspects, kinetics and thermodynamics, must be taken into account simultaneously, especially in the case of reactions carried out under supercritical conditions.

## 6. Experimental techniques for kinetic and thermodynamic data generation

Both kinetic and thermodynamic data are needed to develop and train the theoretical models whichever approach is used. The main features of the experimental techniques and apparatuses required to acquire these data are discussed below. The operating conditions applied in supercritical alcoholysis of lipid resources are available in various bibliographic reviews recently published in the literature, such as Sawangkeaw et al. [38], Stamenković et al. [113], Anitescu and Bruno [25] or Banković-Ilić [35], with Sawangkeaw et al. [38] dealing more specifically with the methanolysis and Stamenković et al. [113] with the ethanolsis. Concerning the phase equilibria mentioned above (Section 4.2), information on the range of temperature and pressure, the nature of the components and phases are summarized in Table 2.

### 6.1. Experimental techniques for kinetic measurements

Most data are acquired in small volume (from 5 cm<sup>3</sup> up to 2 dm<sup>3</sup>) steel reactors that can operate under HT (up to 723 K) and HP (up to 30 MPa). Devices for continuous operation, similarly to an industrial installation, are still limited and most often equipped with tubular reactors (4 m long, 1.5 mm internal diameter [134]), seldom with a CSTR (200 cm<sup>3</sup> reactor [161]), with a sampling system and optionally a sapphire cell for observing phase transitions, all placed at the outlet of the reactor (Fig. 18) [121,134].

Most batch devices are equipped with stirred tank reactors [102,160,226] or tubular reactors [189,198], some with two sapphire windows to observe the phase transitions of the reaction mixture (Fig. 19) [189,198]. These devices usually do not have a sampling system, requiring a quantitative analysis at the end of the reaction. To overcome this drawback new devices have recently been developed; however, they must have a volume large enough so that sampling during the reaction do not disturb the system. Also, they must be supplemented by HP-HT cells equipped with sapphire windows to previously analyze the phase equilibria [163,208,213] (Figs. 20 and 21).

The kinetic data thus generated provide information on the composition of products and unreacted reagents at various reaction times and operating conditions used (temperature, pressure, molar ratio oil/alcohol, and alcohol/cosolvent). The coupling with the simultaneous observation of phase transitions can produce a qualitative understanding of the impact of the thermodynamic behavior of the reaction mixture on the progress of the transesterification and to establish the most favorable operating conditions for the conversion. Due to the batch process, the control of the reaction time (by preheating the reactants and/or a rapid rise in temperature of the reactor, or a quenching of the samples (i.e. samples or reactor)) is necessary to generate realistic kinetic data. Technological advances can improve this procedure.

### 6.2. Experimental techniques for thermodynamic measurements

The equipment used to measure phase equilibria, operating at constant temperature ( $T$ ) or pressure ( $P$ ) and often equipped with sampling devices for compositional analysis of one or several phases in equilibrium ( $x$  and  $y$  for the liquid and vapor phase respectively), is here described. Because various classes of phase equilibria are encountered during the supercritical alcoholysis depending on the considered process unit and relative operating conditions, knowledge of experimental VLE, LLE, VLLE both at LP and HP (and at MT and HT) are relevant to inform either the process simulator directly or the thermodynamic model used to simulate the entire process (Section 4). The last option being most general is actually the “ideal” procedure, especially as this thermodynamic model has the capability, via the EOS on which it is built, to extrapolate the LP phase equilibria information up to the HP conditions that can be found in the supercritical process. Furthermore, thanks to this methodology of model development (EOS-based model informed with experimental data covering a wide range of operating conditions) the same thermodynamic model can be used to simulate the entire process, which significantly helps to consolidate the reliability of the supercritical process simulation.

Devices dedicated to LP-LLE are usually glass jacketed vessels allowing visual monitoring of demixion phenomena and temperature control of the medium, and are equipped with a sampling line for each liquid phase. Beyond the ambient temperature, the lines of transfer must be heated to avoid any risk of demixion of the sampled phases [227–229].

The LP-VLE and LP-VLLE can be studied in two ways.

- The first is ebulliometric method that is well suited to volatile mixtures (Fig. 22). The circulation of the liquid resulting from the condensation of the vapor phase [230,231] allows quickly to reach the equilibrium. This method is not suitable for studying low-volatile mixtures because the mass transfer becomes too weak to reach equilibrium, and is also not adequate to the study of mixtures of components of very different volatility (e.g. water–glycerol, glycerol–ethanol ...).
- The second method, called static method, is well suited to the study of mixtures of low volatile with high volatile compounds.

**Table 2**

Information related to experiments and modeling of phase equilibrium for systems involved in ethyl biodiesel production via the supercritical method with or without cosolvent. Data related to the more extensively investigated alternative via the supercritical method, i.e. methyl biodiesel, are also listed for comparison. Systems related to CO<sub>2</sub> extraction/fractionation of lipidic stocks for pharmaceutical applications are not included here. The UNIQUAC, NRTL, PR, and SAFT models as well as Antoine equation are not predictive and were used as correlation tools.

System	Nature of the phase equilibrium	T/K range	P/MPa range	Experimental information <sup>a</sup>	Modeling information	Reference
Methanol + Methyl laurate	VLE	493–543	2.11–8.49	Yes	None	[188]
Methanol + Methyl myristate			2.41–8.42			
Ethanol + Ethyl laurate	VLE	493–543	2.23–7.09	Yes	None	[190]
Ethanol + Ethyl myristate			2.11–6.93			
Methanol + Methyl laurate	VLE	493–543	2.11–8.49	None	SRK/WS/COSMO-SAC	[195]
Methanol + Methyl myristate						
Ethanol + Ethyl laurate						
Ethanol + Ethyl myristate						
Methanol + C14–C18 methyl esters (methyl myristate, palmitate, palmitoleate, stearate, oleate, linoleate)	VLE	523–573	2.45–1.14	Yes	PR–EOS	[214]
Ethanol + Ethyl stearate	VLE	313–419	0.017–0.098	Yes	NRTL, UNIQUAC and UNIFAC	[215]
Ethanol + Ethyl palmitate		309–422	0.015–9.3			
Methyl oleate + Glycerol	LLE	373–676	0.1	None	GCA–EOS	[189]
Methanol + Glycerol + Methyl oleate		333–423	0.1–0.965			
Methyl oleate + Methanol + Glycerol + Propane	Phase envelopes	400–690	1.0–10.0			
Triolein + Methanol + Propane		400–500	1.0–6.0			
Methyl oleate + Glycerol + Methanol	LLE + VLLE	313–393	0.101–0.512	Yes	GCA–EOS	[182]
Glycerol + Methanol + Methyl oleate	LLE	333–408	0.101	Yes	None	[181]
Glycerol + Monoolein + Methyl oleate	LLE	408				
Ethyl laurate + Ethanol + Glycerol	LLE	323–353	0.101	Yes	CPA–EOS	[204]
Ethyl palmitate + Ethanol + Glycerol						
Ethyl oleate + Ethanol + Glycerol						
Ethyl linoleate + Ethanol + Glycerol						
Ethyl palmitate + Ethanol + Water	LLE	298–333	0.101	Yes	CPA–EOS	[205]
Ethyl oleate + Ethanol + Water						
Ethyl linoleate + Ethanol + Water						
Canola oil FAEE + Ethanol + Glycerol	LLE	303–333	0.101	Yes	CPA–EOS	[202]
Methyl linoleate + Water	Water solubility	288–318	0.101	Yes	CPA–EOS	[203]
FAME from soybean, rapeseed, palm or sunflower oil + Water						
Refined babasu oil + Lauric acid + Ethanol	LLE	303	0.101	Yes	NRTL	[184]
Refined babasu oil + Lauric acid + Ethanol + Water						
Soybean oil FAME + Water + Glycerol	LLE	303–318	0.101	Yes	None	[216]
Soybean oil FAEE + Water + Ethanol						
Castor oil FAME + Water	LLE	303–333	0.101	Yes	UNIQUAC	[217]
Castor oil FAEE + Water						
Castor oil FAME + Glycerol						
Castor oil FAEE + Glycerol						
Castor oil FAME + Glycerol + Methanol						
Castor oil FAME + Water + Methanol						
Castor oil FAME + Water + Glycerol						
Castor oil FAME + Water + Glycerol + Methanol						
Castor oil FAEE + Glycerol + Ethanol						
Castor oil FAEE + Water + Ethanol						
Castor oil FAEE + Water + Glycerol						
Castor oil FAEE + Water + Glycerol + Ethanol						
Jatropha FAME + Water	LLE	303–333	0.101	Yes	UNIQUAC	[218]
Jatropha FAEE + Water						
Jatropha FAME + Glycerol						
Jatropha FAEE + Glycerol						
Jatropha FAME + Glycerol + Methanol						
Jatropha FAME + Water + Methanol						
Jatropha FAME + Water + Glycerol						
Jatropha FAME + Water + Glycerol + Methanol						
Jatropha FAEE + Glycerol + Ethanol						
Jatropha FAEE + Water + Ethanol						
Jatropha FAEE + Water + Glycerol						
Jatropha FAEE + Water + Glycerol + Ethanol						
Jatropha FAEE + Ethanol + Water	VLE	296–342	0.0067–0.0667	Yes	UNIQUAC	[194]
Jatropha FAME + Methanol + Water		283–329				

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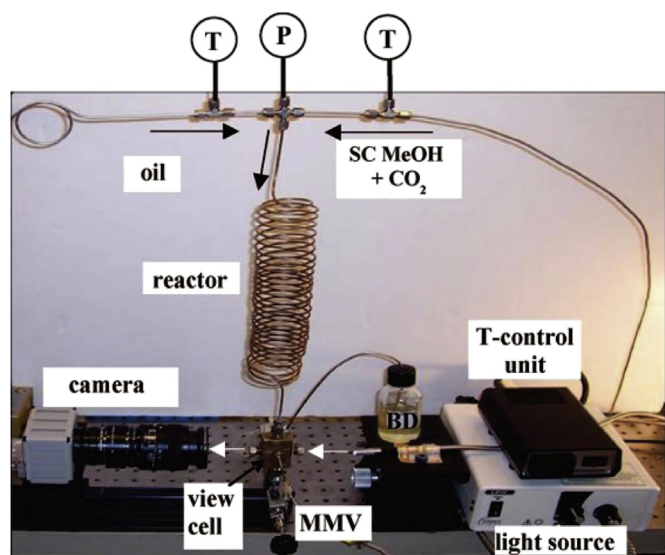


**Table 2** (continued)

System	Nature of the phase equilibrium	T/K range	P/MPa range	Experimental information <sup>a</sup>	Modeling information	Reference
Jatropha FAEE + Ethanol	LLE	295–382	0.101	Yes	NRTL (better) and UNIQUAC	<a href="#">[185]</a>
Jatropha FAME + Methanol		283–361				
Jatropha FAEE + Ethanol + Glycerol		296–343				
Jatropha FAME + Methanol + Glycerol		283–329				
Macauba pulp oil FAEE + Ethanol + Glycerol	LLE	298	0.101	Yes	NRTL (better) and UNIQUAC	<a href="#">[185]</a>
Soybean oil FAEE + Glycerol + Ethanol	LLE	303–333	0.101	Yes	UNIQUAC	<a href="#">[186]</a>
Soybean oil FAME + Glycerol + Methanol						
Soybean oil FAEE + Water + Ethanol						
Soybean oil FAME + Water + Methanol						
Soybean oil FAEE + Water + Glycerol						
Soybean oil FAME + Water + Glycerol						
Soybean oil FAEE + Water + Glycerol + Ethanol						
Soybean oil FAME + Water + Glycerol + Methanol						
Soybean oil FAME + Methanol + Glycerol	LLE	298–323	0.101	Yes	None	<a href="#">[219]</a>
Soybean oil FAME + Ethanol + Glycerol						
Soybean oil FAME + Methanol + Soybean oil	VLE (boiling point)	294–390	0.014–0.092	Yes	None	
Soybean oil FAME + Ethanol + Soybean oil						
Methanol + Soybean oil FAME						
Ethanol + Soybean oil FAME						
Soybean oil FAME + Ethanol + Glycerol						
Soybean oil FAME + Methanol + Soybean oil						
Soybean oil FAME + Ethanol + Soybean oil						
CO <sub>2</sub> + Methanol	VLE	303–343	3.2–11.2	Yes	PR–vdW2 and PR–WS (better)	<a href="#">[220]</a>
CO <sub>2</sub> + Soybean oil FAME	VLE + LLE		1.9–17.3			
CO <sub>2</sub> + Methanol + Soybean oil FAME	VLE		4.2–13.6			
CO <sub>2</sub> + Soybean oil	VLE	313–343	3.76–26.44	Yes	SAFT (better) and PR	<a href="#">[187]</a>
CO <sub>2</sub> + Castor oil			2.12–25.50			
CO <sub>2</sub> + Soybean oil FAEE			1.35–6.01			
CO <sub>2</sub> + Castor oil FAEE			1.77–25.45			
CO <sub>2</sub> + Ethanol + Castor oil			2.13–26.27			
CO <sub>2</sub> + Ethanol	VLE	291–313	N.A. <sup>b</sup>	No	CPA–EOS	<a href="#">[221]</a>
CO <sub>2</sub> + Methanol		291–313	N.A. <sup>b</sup>			
CO <sub>2</sub> + Oleic acid		308	10–70			
Glycerol + Water	VLE	384–481	0.101	Yes	CPA–EOS	<a href="#">[222]</a>
Glycerol + Methanol		350–452				
Glycerol + Ethanol	LLE	363–454	0.101	Yes	CPA–EOS	<a href="#">[222]</a>
Methanol + Glycerol + Methyl oleate		313–373				
Ethanol + Ethyl laurate	VLE	493–523	2.0–7.00	No	CPA–EOS	<a href="#">[201]</a>
Methanol + Methyl laurate			2.0–10.0			
Ethanol + Ethyl myristate			2.0–8.00			
Methanol + Methyl myristate			2.0–11.0			
Ethanol + Glycerol		493–573	2.0–8.00			
Methanol + Glycerol			2.0–13.0			
Methanol + Soybean oil methyl esters		523–573	2.0–12.0			
Ethyl palmitate + Ethyl stearate	VLE	502–520	0.0053	Yes	Wilson, NRTL (better), UNIQUAC	<a href="#">[193]</a>
Ethyl palmitate + Ethyl oleate		502–537	0.0053, 0.0093			
Ethyl palmitate + Ethyl linoleate		514–537	0.0093			
Glycerol + Water	VLE	353–473	0.0062–0.8363	Yes	NRTL	<a href="#">[223]</a>
Ethyl laurate	VLE	420–464	0.00133–0.00933	Yes	Antoine equation	<a href="#">[192]</a>
Ethyl myristate		446–492				
Ethyl palmitate		464–515				
Ethyl stearate		491–534				
Ethyl oleate		486–537				
Ethyl linoleate		486–537				
Ethyl laurate	VLE	313–462	0.18 × 10 <sup>–5</sup> to 0.0085	Yes	Antoine equation	<a href="#">[191]</a>
Ethyl myristate		333–462	0.15 × 10 <sup>–5</sup> to 0.0032			
Methanol + Sunflower oil <sup>c</sup>	Phase transition (VLL–VL–V)	400–670	1.0–35.0	Yes	None	<a href="#">[224]</a>
Methanol + Coconut oil <sup>c</sup>						
Methanol + Methyl oleate						
Ethanol + Sunflower oil <sup>c</sup>	Phase transition (VLL–VL–V)	400–650	1.0–35.0	Yes	GCA–EOS	<a href="#">[225]</a>
Azeotropic ethanol (96°) + Sunflower oil <sup>c</sup>						
Methanol + Methyl laurate						

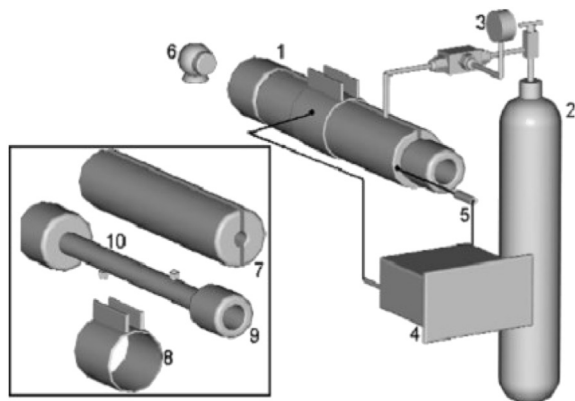
<sup>a</sup> Instruction “Yes” means that the experimental information is provided by the reference mentioned in the table, instruction “No” that the experimental information was taken from another source.  
<sup>b</sup> N.A. – Information not available in the reference.  
<sup>c</sup> Phase transition of reacting systems determined from isochoric lines (global densities: 0.29–0.51 g/cm<sup>3</sup>; molar ratio = 25:1, 40:1).



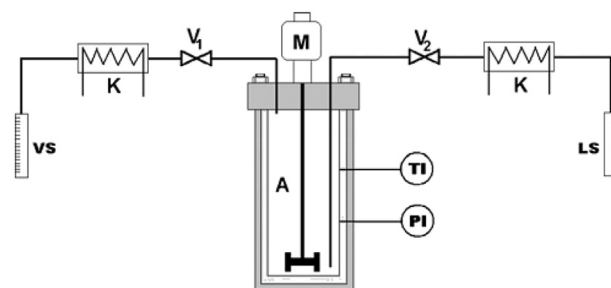


**Fig. 18.** Laboratory flow apparatus to study phase transitions and transesterification reactions. The furnace for the reactor and the heating tapes for the feeding pipes are not shown. Legend: thermocouples (T), pressure indicator (P), micrometric valve (MMV), biodiesel (BD), reactor (Hastelloy pipes of 2 and 4 m in length and 1.5 mm i.d.) [134].

There are two types of static methods: The first is the “classic” TPx which works at different constant temperatures for a given composition of the liquid phase, the composition of the vapor phase being calculated by thermodynamic relations (in the case of binary systems). This method is relatively fast and very accurate in a large pressure range (between a few Pa to few bars) by using a combination of pressure sensors (differential and absolute gages). The most delicate step prior to the pressure measurements is the degassing of the liquid mixture to remove air and volatile impurities (involving important errors when measuring low vapor pressures) without changing the composition of the sample. Ebullition under vacuum with flowing back of the condensed vapor is an effective method for liquid degassing. This static method is well suited to the development of thermodynamic models (determination of binary interaction parameters) [201,222,223,232–234]. The second type is the static-analytical method TPxy in which both vapor and liquid phases are analyzed. This method is well suited to the study of multicomponent systems and is generally used for the



**Fig. 19.** Constant volume batch reactor to study the phase behavior and transesterification reactions using supercritical fluids. Legend: windowed reactor (1), propane tank (2), pressure gauge (3), temperature controller (4), temperature sensor (5); camera (6), aluminum jacket (7); heating tape (8), two windows (9), and stainless steel reactor of 32 cm<sup>3</sup> (10) [198].

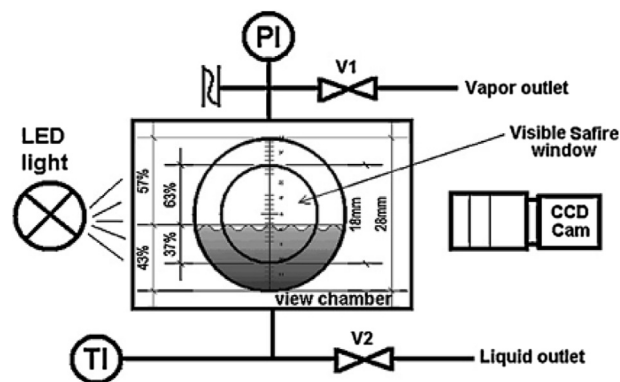


**Fig. 20.** High pressure reactor used for analysis of triglycerides transesterification (capacity: 2 dm<sup>3</sup>). Legend: thermocouple (TI), manometer (PI), autoclave (A), stirrer motor (M), sampling valves (V<sub>1</sub>, V<sub>2</sub>), condenser (K), vapor sample (VS), liquid sample (LS) [163].

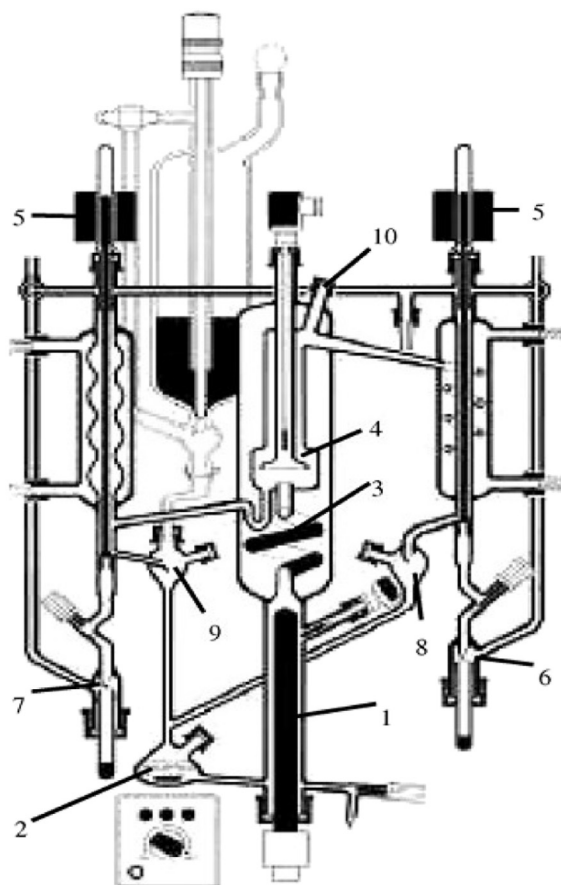
validation of thermodynamic models. However, the commercially available sampling devices for the vapor phase (valves, injectors ROLSI ...) which usually equip the static apparatuses are not suitable to operate at pressures lower than 0.3 MPa. Msakni et al. [235,236] managed to analyze the vapor phase below the ambient pressure and up to 5 MPa by using a system of two six ports pneumatic valves downstream the equilibrium cell (Fig. 23).

Devices dedicated to HP phase equilibria (ScE, VLLE, VLE or LLE) are usually high pressure variable volume equilibrium cell equipped with one or two windows for observation of the cell contents. For a given temperature and system global composition, the set pressure is reached by varying the cell volume thanks to a mobile piston. Sampling lines are provided to determine the composition of the various phases (off-line or on-line), otherwise the composition of a single phase is known and the cell is devoted to phase transition analyses. The mobile piston is also used to keep the pressure constant while sampling. Fig. 24 is an illustration of this class of devices [237].

The need to determine accurately densities together with conditions of phase transitions of reacting systems under HT and HP (see Section 5) led recently some researchers to conduct experimental studies based on an isochoric method which does not require direct observation of the occurring phenomena [224,225]. Via this technique, variations of pressure and temperature are recorded for a mixture of known mass and composition introduced in a closed constant-volume cell (Fig. 25). Thus, knowing the mixture global density with a high precision, phase transition points are obtained accurately from the intersection of the pressure vs. temperature isochoric lines (whose slope changes abruptly with the change of the system phase number, Fig. 26).



**Fig. 21.** High pressure, high temperature view chamber to study phase equilibrium (capacity: 27 cm<sup>3</sup>, maximum operating conditions: 35 MPa, 473 K). Legend: pressure indicator (PI), temperature indicator (TI), valves (V<sub>1</sub> and V<sub>2</sub>) [213].



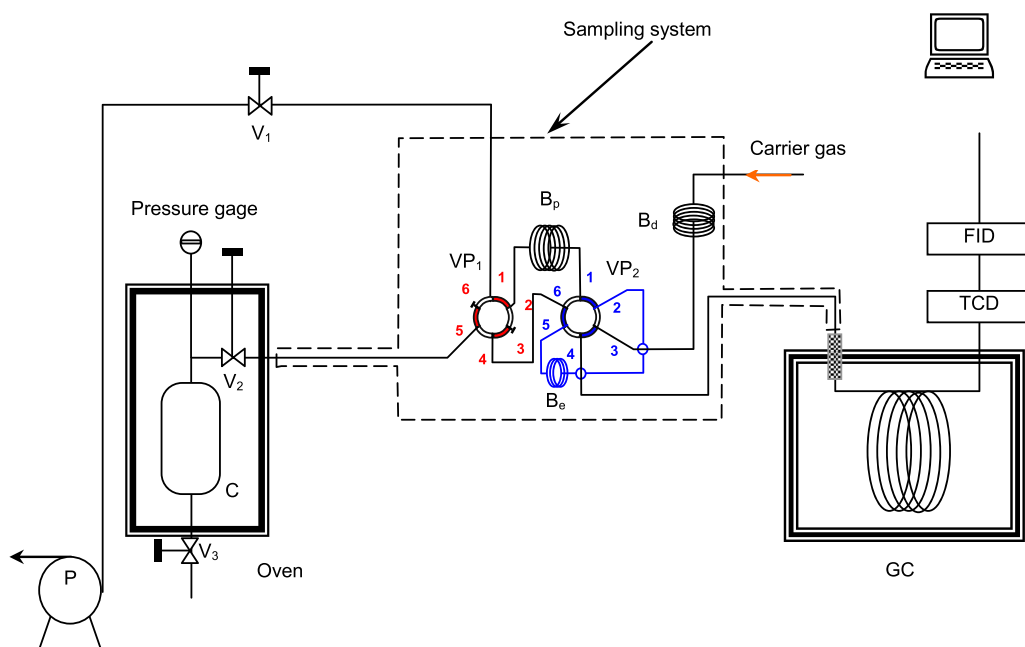
**Fig. 22.** Ebulliometer with dynamic recirculation of the vapor and liquid phases (Labodest®). Legend: (1) electrical immersion heater, (2) mixing chamber, (3) contact path, (4) separation chamber, (5) solenoid valves, (6) vapor phase, (7) liquid phase, (8 and 9) circulation streams, (10) sampling port [230].

### 6.3. Suggestions for future developments of experimental techniques for thermodynamic and kinetic measurements

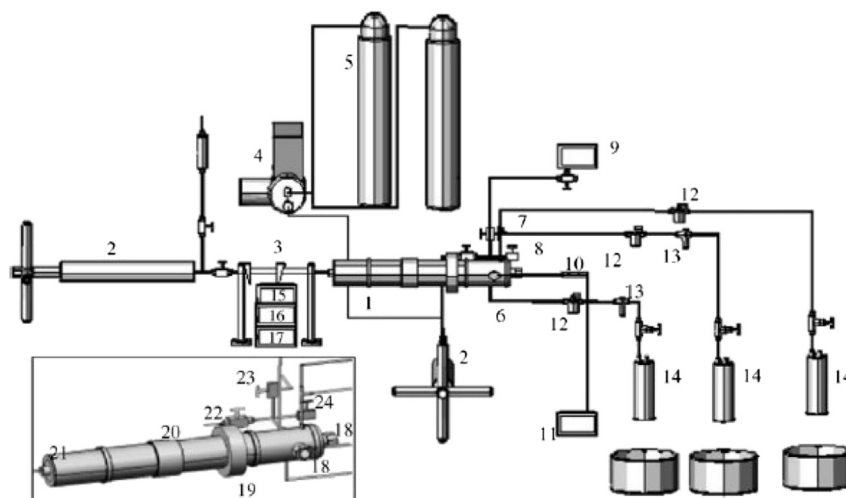
The development and operation of low pressure static devices (TPx and TPxy from  $10^{-6}$  to 0.2 MPa) represent a technological challenge that few laboratories were able to overcome. In addition, a multifunctional device “Reactor & HT-HP equilibrium cells” with sampling and quantification of the different species present in the medium (reactants (triglycerides, alcohol), cosolvent ( $\text{CO}_2$ ), intermediate products (mono- and diglycerides) and final products (biodiesel)) would constitute a scientific and technological advance. It would establish, whatever approach is used, a model coupling the kinetic phenomena, phase equilibria and chemical equilibria present in the process reaction unit. Such a device, which would be a synthesis of those shown in Figs. 18–24, with a sapphire reactor placed in a furnace equipped with an observation window, should be developed to support further progresses in the thermodynamic and kinetic modeling of supercritical transesterification.

### 7. Exhaust emissions of biodiesel still being questioned (while storage, transport and engine performance are well understood)

This section gives a synthetic overview of the observed impacts of biodiesel on exhaust emissions and of the alternatives proposed to reduce them. Discussion with insight of the relation between chemical structure, physical properties and emissions will be conducted at the macroscopic scale (similarly to an input–output material balance). Hence, and as mentioned in the main highlights of the present work (Section 1.2), the reader is invited to refer to a previous work [42] and to Westbrook’s review [43] for further detailed information on combustion of biodiesel and related compounds with phenomena prediction via chemical kinetics (experiments and modeling), and to refer to the reviews by Kohse-Höinghaus et al. [40] and by Westbrook [43] for complementary information related to ethanol biofuel.



**Fig. 23.** Static-analytical device for low pressure VLE and VLLE measurements with on-line analysis of the vapor phase. Legend: ( $V_{1,2,3}$ ) valves, ( $VP_{1,2}$ ) pneumatic valves, (C) phase equilibrium cell, ( $B_{e,p}$ ) sampling, venting loop, (P) pump. To sample the vapor phase, vacuum is first applied to the sampling loop,  $B_e$ , via valve  $VP_1$  and  $V_1$  ( $V_2$  closed). Once the gas sampled from the cell ( $V_2$  opened), it is swept and injected into the GC thanks to the carrier gas. The use of a capillary column with low inner diameter minimizes the sampling volume of the vapor phase inducing very low or quasi inexistent changes in composition of the liquid phase during the vapor phase sampling [235,236].



**Fig. 24.** Experimental device for high pressure phase equilibria measurements (LLE, VLE, and VLLE). Legend: (1) equilibrium cell; (2) manual pressure generator; (3) position sensor; (4) compressor; (5) CO<sub>2</sub> and propane cylinders; (6) heavy liquid phase sampling line; (7) vapor phase sampling line; (8) light liquid phase sampling line; (9) pressure sensor; (10) temperature sensor; (11) temperature register; (12) Rheodyne valves; (13) oil traps; (14) gas volume measuring device; (15) temperature register and control; (16) magnetic stirrer control; (17) position sensor control; (18) view window; (19) magnetic stirrer; (20) heating tapes; (21) aluminum casing; (22) solvent feed valve; (23) oil feed valve; (24) purge valve [237].

### 7.1. Main reasons for this controversy

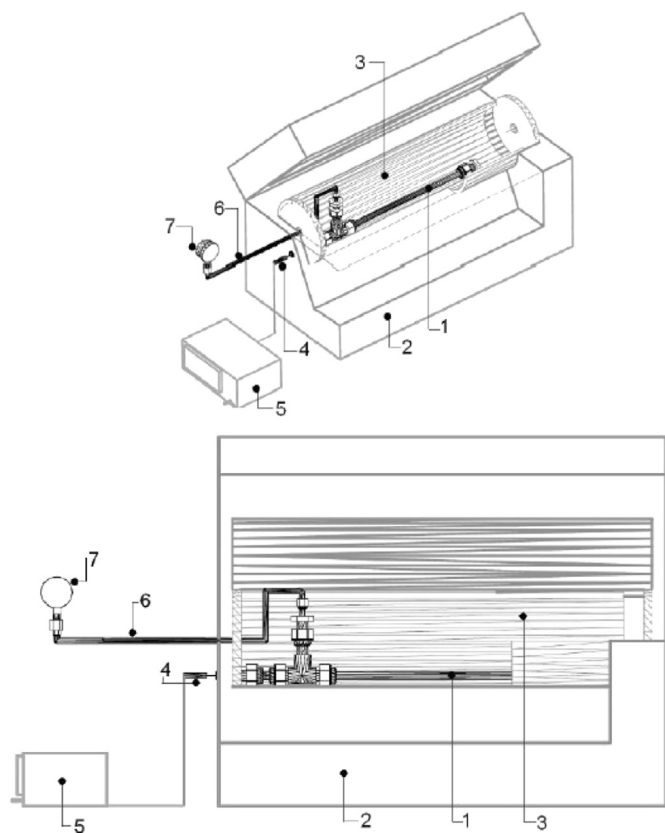
Many studies aiming at assessing the biodiesel emissions generated during combustion show large differences [238–247]. These mainly come from a lack of reference frame, making any result comparison difficult, with large differences in terms of:

- Engine technology and after-treatment performances (Euro level), for both vehicles and power generators,
- Test procedure (engine test bench, chassis dynamometer testing or real road operation conditions),
- Biodiesel composition (that depends on the nature of raw materials and on the starting oil purity level),
- The precise biodiesel blend (with petrodiesel) used.

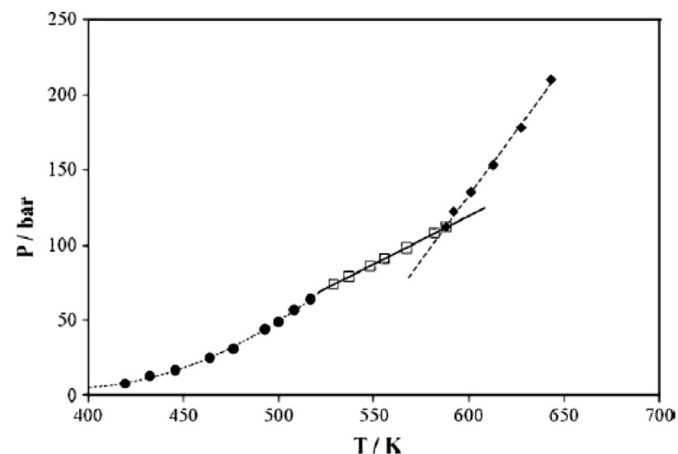
Most researches are carried out on engine test benches or chassis dynamometers [238,242,243,247–249]. By contrast, studies of biofuels blends in power generators [250,251] or vehicles on real road operation conditions are scarce [252].

### 7.2. Main features regarding regulated and non-regulated emissions of biodiesel

To evaluate the sustainability of a fuel alternative, it is important to consider its impacts on both the regulated emissions (NO<sub>x</sub>, PM, HC, and CO) as well as the non-regulated ones (such as carbonyl



**Fig. 25.** Scheme of the isochoric apparatus: (1) constant-volume cell, (2) electric oven, (3) aluminum foil, (4) temperature sensor, (5) process control equipment, (6) silicone line, (7) pressure gauge [224].



**Fig. 26.** Pressure vs. temperature for ethanol-sunflower oil (molar ratio = 40:1, global density = 0.44 g/cm<sup>3</sup>). Legend: (●) Vapor pressure line, (□ and solid line) vapor–liquid region, (■ and dashed line) single phase region [225].

compounds, polycyclic aromatic hydrocarbons) which are equally harmful and thus more dangerous if accumulated without control.

In spite of the problems identified in Section 7.1, some conclusions achieved wide recognition (with the exception of Fontaras et al. work [242] that should be validated): the inclusion of methyl biodiesel in petrodiesel (7% for diesel fuel distribution) leads to a reduction in the formation of CO, HC, and in the mass of soot emitted, due to a higher oxygen content (leading to a more complete combustion of biofuel) and the absence of sulfur and aromatic compounds [238,241,244–248,253–258]. It should also be noted a slight but significant improvement of 1–2% in CO<sub>2</sub> emission observed during the combustion stage of B5 and B30 blends with the Artemis European driving cycles [244]. This reduction is however accompanied by an increase in the number of ultrafine PM (less than 0.1  $\mu\text{m}$  diameter [259,260]) with widely recognized adverse effects on the environment and health. This increase in PM number and the evolution of the particle size distribution is attributed to a modification of the PM composition due to an increase of the soluble organic fraction (SOF) modifying thus the nucleation mode [249].

Nevertheless, emissions of NO<sub>x</sub> (precursors of photochemical formation of tropospheric ozone and smog) during the combustion of biodiesel compared to petrodiesel remained for a long while subject to controversy [41,42,261]. One reason for this controversy is that NO<sub>x</sub> emissions are related to the combustion phenomena by chemical factors (i.e. fuel composition) but also by physical (i.e. associated to component parts of the engine as the angle of the spray nozzle of the fuel in the combustion chamber). Experimentally, it was observed that an increase in the length of primary aliphatic chain of the fatty acid ester or its degree of saturation, or the chain length of the alcohol, lead to a significant NO<sub>x</sub> reduction [41,42,239,245,262]. McCormick et al. [263] who studied NO<sub>x</sub> emissions generated by the combustion of 21 different fuels (petrodiesel and biodiesel) from a six cylinder, four stroke engine, showed that linear relations can be applied between NO<sub>x</sub> emissions and density, cetane number or iodine number. According to these authors, the increase of NO<sub>x</sub> emission with a decrease of cetane number is attributed to an increase of the ignition delay and thus an increase of the temperature inside the combustion chamber. Other studies [264–266] proposed that the increase of oxygen content in the biodiesel composition is favorable to NO<sub>x</sub> emissions. In addition, adjustments to engine tuning (particularly at the injection and exhaust gas recirculation, EGR) could also help to reduce NO<sub>x</sub> emissions [41,42,258,267], but at the expense of an increase in soot production in most cases [268]. Recent works highlighted some strategies effective at simultaneously reducing NO<sub>x</sub> and soot (such as a combined use of EGR and multiple injections or the in-cylinder EGR stratification) [269,270].

Concerning carbonyl compounds (i.e. aldehydes and ketones), studies to date (fewer than those for regulated pollutants) do not allow concluding clearly about the impact of biodiesel on these emissions which are precursors of the same class of air pollution as NO<sub>x</sub> and, for certain (the light aldehydes) also mutagenic and/or carcinogenic. Some controversial findings (decrease in carbonyl emissions in some cases and increase in others) have highlighted the strong influence of the type of engine used for a same biodiesel [267,271–274] or of the type of biodiesel used for a same engine [243]. Also, studies conducted with a diesel passenger car operated over the New European Driving Cycle (NEDC) and the Artemis cycles reported significant increases of carbonyl emissions for biodiesel/petrodiesel blends compared to petrodiesel fuel. Even higher levels of carbonyl emissions were observed when using oxidized biodiesel blends prepared from soybean WCO, probably because of the presence of cyclic acids in the starting lipid-based feedstock resulting from the frying process [275,276].

Other specific pollution diesel engines, namely polycyclic aromatic hydrocarbons (PAH), known carcinogens and mutagens, raise serious concerns about the increase in the rate of incorporation of biodiesel, and have sparked recent work to assess the impact of these new fuels on PAH emissions [277,278]. Tests performed on a real vehicle over the NEDC and Artemis cycles confirmed that PAH emissions depend (similarly to other emissions discussed above) on the load and driving speed of the vehicle, the type of engine and the chemical structure of biodiesel (the rate of PAH formed increasing with the biodiesel unsaturation). Particularly, it was observed that the addition of biodiesel led to increases in low molecular-weight PAH and to reductions in large PAH having the most harmful activity [278]. Furthermore, as for the carbonyl pollutants, the use of WCO methyl esters as biodiesel had a more negative impact on the PAH emissions than methyl esters prepared from the same virgin oil, probably because of the presence of polymerization products in the WCO [275,276]. These observations, together with positive results obtained by some other researchers who investigated pure WCO biodiesel emissions [246], demonstrate clearly that the purification steps during biodiesel production need to be carried out properly.

Also, in addition to an engine tuning (e.g. EGR, injection system), optimizing the fuel formulation for a more efficient and cleaner combustion should be considered simultaneously [268].

### 7.3. Methyl biodiesel vs. ethyl biodiesel

Concerning emissions, other controversies also exist regarding the advantages of ethyl biodiesel (FAEE) compared to methyl biodiesel (FAME). Most results in diesel engines suggest a positive environmental balance for FAEE with lower emissions of NO<sub>x</sub>, PM, CO and THC [239,241,279], and far fewer ultrafine PM (the most harmful) than for FAME. Nevertheless, recent fundamental studies conducted in flames of biodiesel surrogates showed that short ethyl esters (C4–C5) exhibit a somewhat higher sooting propensity compared to methyl esters with similar carbon number, but differences diminish significantly with increasing length of the aliphatic main chain (esters investigated up to C12) [280]. Regarding NO<sub>x</sub> formation, no significant difference was observed between flames of methyl and ethyl esters, whatever the length of the aliphatic main chain [281]. In contrast, higher emissions in carbonyls (acrolein, propanal, acetone) were observed with FAEE than with FAME [250,251].

In addition, it is unanimously recognized that FAEE have better biodegradability, higher flash point, improved cold-flow properties and oxidation stability, making them a safer fuel for storage and transportation than FAME [29,42,238–241,282]. Moreover, whatever the origin of the lipid resource used to produce them (refined edible oils [283], NEVO [241,284], WCO [239,240,248,253,254,256] or WFO [285,286]), FAEE showed similar physicochemical properties if the purification steps are carried out properly [93,250,251].

Finally, the use of biodiesel (FAME or FAEE) does not lead to a significant loss of power except at high engine speeds; however, an increase in fuel consumption is recorded to offset the lower calorific value of biodiesel compared to petrodiesel [238].

### 7.4. Effect of residual ethanol in biodiesel–petrodiesel blends

Ethanol has been proposed as an additive to improve biodiesel key fuel properties (viscosity, cloud and pour points), without affecting adversely the oxidation stability and corrosiveness of the biodiesel–petrodiesel fuel blend if ethanol is introduced in low concentration (6%) [287,288]. Nevertheless, ethanol–biodiesel–petrodiesel blends show higher brake specific fuel consumption than petrodiesel [289]. Regarding combustion, it was observed that



the use of ethanol–biodiesel–petrodiesel fuel blends have a clearer benefit in terms of soot emissions in mass than conventional biodiesel–petrodiesel blends with the same oxygen content [290]. This result is in agreement with chemical kinetic studies concluding that the alcohol functional group is more effective in inhibiting soot formation than the ester group [138]. Other chemical kinetic studies have also shown that blending ethanol (or other alcohols) with petrodiesel led to a retarded ignition of the fuel blend by scavenging radicals and inhibiting the low-temperature chemistry of the hydrocarbons [291–293]. Nevertheless, the small amounts of ethanol introduced in the blends should not deteriorate the cetane number significantly [292]. CO and HC emissions increased with ethanol concentration in blends (from 10 to 20%), while NO<sub>x</sub> emissions are decreased [289]. These results were also observed by a research team who carried out an experimental campaign in a Euro 5 automotive diesel engine with ethanol (20%)/rapeseed methyl ester (10%)/petrodiesel (70%) blends (all % given by volume) [294].

#### 7.5. Effect of residual water in ethanol–biodiesel–petrodiesel blends

The effect of addition of water-containing ethanol in biodiesel–petrodiesel blends was also investigated in a diesel-fueled engine generator [295]. Due to more complete combustion and lower reaction temperature via the water quench effect, fuel blend of water-containing ethanol (4%vol)–biodiesel (10%vol)–petrodiesel (85%vol) and butanol (1%vol) used as cosolvent demonstrated good energy performance and significant reduction of PM, NO<sub>x</sub>, and total PAH. Biodiesel (soybean FAME) acting as stabilizing agent produced a blend of fuel with an adequate integrity in terms of miscibility, phase stability, viscosity and heating value [295]. It should be noticed that a positive effect of water addition on NO<sub>x</sub> reduction has also been reported for diesel engines running with methyl biodiesel blend (20 mol% tobacco seed oil FAME, 80 mol% petrodiesel, fuel blend injections with a steam-to-fuel ratio of 20 wt%) with an additional improvement in the engine performance (increased power and efficiency with a decreased specific fuel consumption) [296,297].

#### 7.6. Suggestions for future refinements related to formulating cleaner biodiesel fuel

Based on the results discussed above the addition of anhydrous or hydrated bioethanol should be encouraged in the formulation of biodiesel–petrodiesel fuel blends. Furthermore, using ethyl biodiesel in this blend rather than methyl biodiesel is more efficient since crude ethyl biodiesel may carry some bioethanol from the production process. Models should be developed for establishing optimal blends aimed at improving the system profitability for some defined production costs, market demand, and fuel prices while meeting multiple property requirements (such as kinematic viscosity, density, lower heating value, cloud point, cetane number, fuel stability, and sulfur content) [298]. In addition the quality of emissions could also be included as supplementary criteria using predictive chemical kinetic models [42,299,300].

While the use of biofuels is highly encouraged by the EU, a number of environmental questions still remain. It is therefore essential to provide a decisive characterization of pollutant emissions (especially PM, PAH, NO<sub>x</sub> and carbonyls) from the combustion of biodiesels and to test the effectiveness of commercial post-treatment cleanup systems. Recent studies have addressed these questions by testing on a diesel power generator two biodiesel fuels mixed with petrodiesel (soybean oil methyl esters and WCO ethyl esters) and showed the inefficiency of commercial emissions-

control systems mounted on the engine in terms of ultrafine PM and carbonyls [250,251]. Such studies should be pursued with various pollution control systems and other types of biodiesels mixed with bioethanol (and petroleum diesel) to confirm these results. Moreover, since the conclusions are affected by the nature of the biodiesel studied (i.e. lipid resource and alcohol used on its production), the biodiesel must be clearly characterized and blended with petrodiesel in well defined proportions before admission into the engines. In addition, studies should be conducted using the same well-defined standard, with different types of engines placed under real operating conditions (actual vehicle for transportation and power generator for the deployment of cogeneration).

### 8. Technological flexibility of the supercritical process to a diversification of resources

In addition to the two-step process (hydrolysis/esterification) of Saka–Dadan (Fig. 6, Section 3.4), other alternatives using supercritical fluids have been adopted to convert various resources (fats and alcohols). Three of these alternatives devoted to biodiesel production (one from lipid wastes and two from algal biomass) are outlined below.

#### 8.1. Hydrothermal partial oxidation of fatty acids

This reaction pathway [301,302] (operating at 573 K, 9–10 MPa with 35%vol H<sub>2</sub>O<sub>2</sub> solution) has demonstrated the possibility of converting unsaturated compounds with long hydrocarbon chains in compounds with shorter chains (by oxidation cleavage mainly at the CH=CH double bond). Tested on oleic acid as surrogate molecule of FFA (its alkyl chain with 18 carbon atoms contains a CH=CH double bond in position 9), various products having predominantly 9 carbon atoms have been isolated: aldehydes, carboxylic acids and di-carboxylic acids, as well as bi-functionalized molecules with aldehyde and carboxylic groups (the carbonyl groups being always positioned at the chain end). This application addresses the improvement of cold flow properties of biodiesel by decreasing the molar fraction of saturated molecules with long alkyl chains.

This reaction pathway could also be considered for WFO, which, without pretreatment, lead to an inefficient biodiesel fuel and pose storage problems which are due to poor oxidation stability related to the large number of unsaturated bonds (up to 6) in longer alkyl chains (up to 22 carbon atoms). Furthermore, similarly to the supercritical transesterification a cosolvent could be used to reduce the severity of the reaction. The CO<sub>2</sub> would be a good candidate because it should favor the production of dicarboxylic acids. This new way of hydrothermal conversion via partial oxidation in presence of CO<sub>2</sub> could also be applied to the WFO or WCO with high levels of water to generate bio-based monomers with several chemical groups at the chain end (dicarboxylic acids, bi-functionalized molecules: aldehyde and carboxylic acid).

#### 8.2. “Lipid extraction by thermochemical liquefaction of microalgae and *in situ* supercritical ethanolysis” vs. “subcritical hydrolysis and *in situ* supercritical esterification/ethanolysis”

Two major types of processes for the production of biodiesel from microalgae using supercritical ethanol have been proposed in the literature.

- The authors [303] describe the first process as a thermochemical liquefaction of microalgae (*Spirulina*), containing about 4 wt% water, with *in situ* transesterification of their lipids. Both thermochemical processes (liquefaction and transesterification) are



carried in a single step in an autoclave with supercritical ethanol ( $T/K$ : 553–653, solid (algal biomass) to liquid (ethanol) ratio (g/mL): 0.02–0.13, liquid filling ratio (volume of ethanol/volume of autoclave, %): 10–30,  $P/MPa$ : 6.9–11.4, Fig. 27) [303]. After filtration and evaporation, the recovered liquid fraction (referred to as “bio-oil”) contains mostly FAEE. Mass yields of “bio-oil” up to 45% are obtained and can be improved (up to 57%) through the use of a catalyst (iron sulfide II (FeS) in concentrations between 5 and 7 wt%).

- The second type of process produces ethyl biodiesel (FAEE) from fresh microalgae (*Chlorella vulgaris* containing 1–2 wt% FFA and about 80 wt% water) by combining two successive steps similar to the Saka–Dadan thermochemical process (Fig. 6). The first step is a subcritical hydrolysis of the intracellular lipids at 523 K (for 15–60 min), followed by filtration to remove the nutrient-rich aqueous phase from the solid phase containing lipids essentially as FFA (80–90% of the lipids originally present in the algal biomass). The second step is the esterification of the FFA by supercritical ethanol ( $T/K$ : 548–598, solids to ethanol ratio (wt./wt.): 1:8–1:2, reaction time/min: 60–120) and the transesterification of TG, DG and MG, not hydrolyzed in the first step, into FAEE with a yield of around 56 wt% (Fig. 28) [304].

Other research teams have proposed variants aiming at optimizing the process of wet microalgae conversion (80–90 wt% water) in a single step with extraction of lipids from microalgae via liquefaction catalyzed by subcritical water contained therein, and *in situ* methanolysis under:

- either supercritical conditions ( $T/K$ : 528, wet algae to methanol ratio (g/mL): 1:9, reaction time/min: 25,  $P/MPa$ : 8.3, for the *Nannochloropsis* strain containing 90 wt% water and producing essentially methyl oleate [180]),
- or subcritical conditions ( $T/K$ : 448, wet algae to methanol ratio (g/mL): 1:4, reaction time/min: 240,  $P/MPa$ : 3.5, for *C. vulgaris* containing 80 wt% of water and producing mainly methyl palmitoleate [70]).

The main advantages of the second category of processes compared to the first are the absence of catalyst and the fact that it operates directly on a wet material, which reduces both energy and equipment required for drying the algal biomass. Furthermore, nutrients (e.g., N and P) and glycerol from processed biomass can be captured in a sterile aqueous phase free of catalyst and then reused

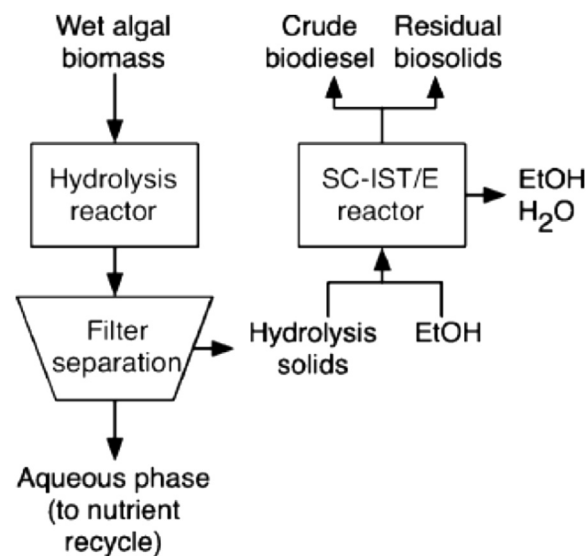


Fig. 28. Main stages for biodiesel production from wet algal biomass (*Chlorella vulgaris*) by intracellular hydrolysis and supercritical ethanolysis of lipids [304].

for algal cultivation, reducing even more the impact of biodiesel production via this route.

Hence, this alternative of *in situ* production of algal ethyl biodiesel via subcritical hydrolysis and supercritical esterification/ethanolysis would deserve to be considered using  $CO_2$  as a cosolvent to reduce the severity of the reaction conditions. Also, it would be worth of integrating a heat exchanger network [136] or a cogeneration unit producing energy (heat and electricity) from materials (algae residues, crude glycerol) in order to improve the energy balance [134]. In addition, a preliminary step of mechanical pre-concentration (partial removal of water) could even be considered upstream of the process to reduce the amount of water present in the hydrolysis step. This step of pre-concentration should not be confused with the microalgal culture dewatering. Indeed, the latter is a major obstacle to industrial-scale processing of microalgae for biofuel and other high-value biochemical productions due to the very dilute nature of harvested microalgal cultures, resulting in high energy consumption required for dewatering [71,73].

## 9. Life cycle analysis (LCA) of supercritical biodiesel

### 9.1. A framework to define and the data to obtain to ensure the most reliable result

In accordance with the European Directive 2009/30/EC (Section 1), recent studies published on biodiesel LCA tend to use approaches as broad as possible, from the resources production and conversion, to the fuel combustion [24,95,305–308].

In order to obtain information about the input/output of materials and energy in the process considered, and eventually compare its performance with other alternatives, most of these LCA were coupled with process simulation [95,141,305,306]. Nevertheless, thermodynamic and kinetic models with limitations have been used during this stage (Section 4), leading to simulation results which may deviate from reality, especially for the supercritical method (Section 5). Moreover, none of these works investigated a supercritical process flowsheet combining any solutions that would significantly improve LCA (Section 3.4).

The main evaluation criteria taken into account in typical LCA are technical and economic assessments (including the need for

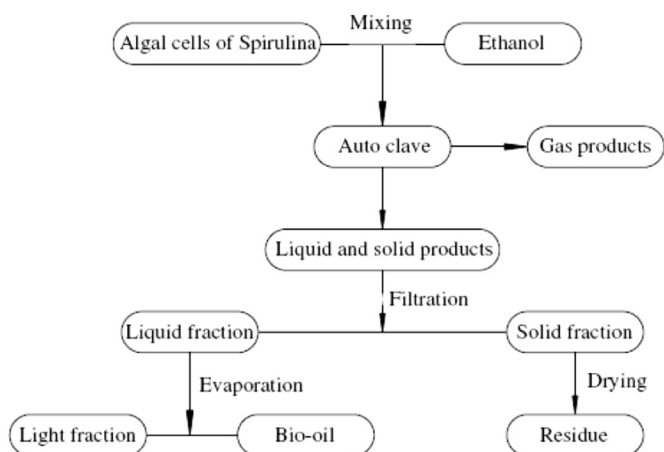


Fig. 27. Main stages for the production of bio-oil (FAEE as major components) by thermochemical liquefaction and *in situ* transesterification of wet algal biomass (*Spirulina*) with supercritical ethanol [303].

non-renewable primary energy) and environmental (mainly accounting for GHG emissions). Some studies have sought to include other impacts (such as human toxicity, aquatic and terrestrial ecotoxicity, eutrophication, acidification, land use... [141,306,309].), but their results highlighted the lack of information and of reliable models for the evaluation of these impacts. In particular, the methods of calculating the impacts related to human toxicity and ecotoxicity can lead to different results [310], and the same is valid for the methods accounting for GHG emissions on an entire industry [3]. In addition, safety and social impacts associated with technological risks have been scarcely recognized in LCA [311], which is a drawback for HT-HP processes.

Furthermore, local situations (such as variations of crop types and yields in function of the geographical area) should also be considered as they can influence the LCA outcome [309,312,313].

In such circumstances, it is understandable that researchers [311,314] claim the problem of extensive development of biodiesel is not easy to tackle when all the aspects (technical, environmental, social, economical, and even safety) should be considered. Nevertheless, this is the most reliable methodology for having a chance to isolate a sustainable synthesis pathway for biodiesel generation; especially as the considered route is a new process which is still not constructed and can thus be analyzed from the beginning.

Hence, LCA combined with process design and simulation/optimization in order to search for sustainable alternatives of biodiesel production still requires improvements, although extensive work on this challenging topic has already led to advanced knowledge. These improvements are all the more important that LCA cannot guarantee its verdict on the viability and sustainability of a sector if the databases and the required impact assessment models are not themselves reliable.

## 9.2. Suggestions for future refinements of biodiesel LCA

A tool for decision support on potential renewable energies, based on a multi-criteria methodology, would lead a more comprehensive, and therefore more realistic, assessment of the biodiesel production by supercritical ethanolysis of TG (whatever their origin). This tool is especially necessary because recent LCA studies comparing various methods of producing biodiesel by methanolysis of WCO (based on process simulation, but, as discussed above, not necessarily with appropriate thermodynamic models) are controversial in terms of the process energy balance via the supercritical route (negatively evaluated [98,99]), while the environmental impact found an unanimous positive assessment [38,39,66,95,100,311]. However, these studies have not integrated cogeneration heat–mass–electricity (Fig. 7) which should improve this criterion [315,316], especially if the capacity of the production unit is optimized using the LCA [24,96]. The differences between the cropping systems for perennial (such as sugarcane) and annual (such as sugar beet, rapeseed, corn, soybean, sunflower, etc) should be considered in more details [317] as well as the potentialities of crop rotation [318]. The allocation of impacts between the main products (sugar in the case of sugarcane) and the wastes (molasses for example) remains a source of discussion.

For sustainability assessments of production chains, the concept of exergy has been used in complement to energy balance to take into account the quality of energy and the losses of useful energy (irreversibility) in the product life cycle [24,319–323]. Therefore, exergy is considered a better instrument for life cycle and process analysis than energy, and should be used for the sustainability assessment of the biodiesel life cycle produced via supercritical TG ethanolysis. In addition, the irreversibility of the life cycle of biodiesel supplied by the exergy of the system could be used to assess

the biodiesel energy sustainability using the exergy return on investment (ExROI) concept which calculates the ratio of the exergy that the biodiesel contains to non-renewable exergy consumed in the system (exergy cost) [24]. However, as its conceptual definition does not take into account other factors than exergy (such as potential deforestation, pollutant emissions, etc.), ExROI is not a measure of the global sustainability of a fuel, but only from an energy perspective (energy sustainability). Thus, it is not surprising to observe during assessment of fuel obtained via different routes that the biodiesel with the highest ExROI (so the most sustainable from an exergy point of view) has the highest GHG emissions (thus, is less sustainable from the climate change point of view) [24]. As a result, it is important that among the various impacts accounted for, the human toxicity and ecotoxicity due to combustion emissions in the diesel engine of the produced biofuel (methyl biodiesel vs. ethyl, in the presence or absence of anhydrous ethanol or not) are considered.

The design of experiments (DOE) has been successfully applied to identify the relevant parameters of a complex process and optimize their values [324,325]. This approach could be adopted and extended to any system whose complexity lies in the absence of explicit analytical models to describe its behavior. Thus, in the absence of reference, the optimal production capacity of supercritical biodiesel could be determined by combining “Design of Experiments & Process Simulation/Optimization & LCA” where experiments will be performed virtually via process simulation. Hence, it would be more accurate to talk about “design of numerically-generated experiments” or more concisely “numerical design” [325]. After selecting some operating parameters considered as important for the process (factors) and defining domain of variation for each of them, process simulation would generate the outputs of materials and energy/exergy allowing estimation of the selected key variables for the evaluated sector (responses). Among factors (reactor temperature and pressure, input flowrate of alcohol and CO<sub>2</sub>, etc.), production capacity and nature of feedstocks could also be selected; examples of responses might be ExROI, effluent flowrates, operating and equipment costs, etc. Then, response surface methodology (RSM) would allow predicting the responses over the whole domain defined for the factors, analyzing their simultaneous influence on the responses, and showing their optimal values from isoresponse curves yielding the desired responses (minimized for some or maximized for other). Multicriteria optimization based on the desirability function can possibly be used in order to estimate a domain of compromise in which the factor optimal values converge simultaneously toward acceptable values for the responses [325]. Screening of the obtained process alternatives by LCA (integrating also ecological, societal and security impacts) would yield in principle a potential sustainable alternative of the biodiesel production process. An iterative procedure by changing the selected factors and keeping those identified as the most relevant during the previous iteration could be probably necessary. Furthermore, while the method of biodiesel production will be unchanged, the configuration of the process might change after optimization via recycles of flows of materials and/or energy/exergy, which would increase the number of simulations. Therefore, the coupling DOE-RSM is a particularly pertinent tool as it minimizes the number of simulations. Moreover, the boundaries of the investigated system could be enlarged beyond the resource conversion process into biodiesel by including the combustion stage, which offers the advantage of performing/evaluating simultaneously process and product formulation to define the most sustainable alternative sector. In that case, responses of the numerical design would be generated “numerically” via simulation for parameters related to the process (like previously). However, parameters related to emissions would be generated

“experimentally and/or numerically” via combustion study of the produced fuel in diesel engine. Numerical information would be obtained via kinetic models of combustion combined with techniques based on computational fluid dynamics [42], and possibly models developed for formulating of clean biofuels (Section 7.6). Moreover, the coupling DOE-RSM might be used for limiting the number of combustion experiments, and thus the consumption of fuel required for achieving the entire design (in addition of identifying the most relevant factors with their optimal values leading to the desired responses: minimum exhaust emissions and maximum engine performance).

## 10. Suggestions for new R&D directions to supercritical ethanolysis

Based on the various issues reviewed on this work, suggestions for new R&D directions aimed at developing a “BioDiesel Sc-BioEt/CO<sub>2</sub>-TG alternative that would be Sustainable for Human and Environment” (BioD-SHE) are proposed. Their main features are summarized in Figs. 29 and 30, with further details in Tables 3 and 4. Thus, the BioD-SHE alternative, based on the supercritical (Sc) alcoholysis process of lipid resource (TG) with bioethanol as alcohol and CO<sub>2</sub> as cosolvent (Sc-BioEt/CO<sub>2</sub>-TG) and integrating glycerol valorization and cogeneration (CHP), should be a responsible and feasible alternative to 2G&3G biodiesels by its intrinsic characteristics, including:

- Key vectors of motivation (i.e. man and his environment),
- Diversity of potential bioresources leading to a biodiesel 100% “biobased and renewable” using for lipid source: NEVO, agri-food waste such as WFO or WCO, or pre-concentrated algal biomass; And as alcoholic source: bioethanol from agricultural residues such as grape marc, molasses or sugarcane bagasse,

while dedicating the finest raw materials to the food and health sectors,

- A modular and flexible process allowing the use of a diversity of resources by changes in operating parameters, and with lower equipment costs,
- Lower specific emissions from the combustion of biodiesel products (aldehydes, ketones, ultrafine PM, NO<sub>x</sub> and PAHs),
- The overall assessment of the sector “resources–conversion–engine emissions,” based on an integrated approach “multi-scale modeling/simulation/experimental validation/optimization/LCA” to meet the 3E criteria (eco-design/eco-material & energy/eco-pollutants) while recognizing the ecological, societal and security impacts via LCA.

In addition, the BioD-SHE approach is based on the idea that a solution to the “post-oil” age requires to satisfy “techno-diversity & biodiversity” [20]. Thus, it proposes an alternative to the 2G&3G biodiesel production, applicable to short, medium and long term, based on the bioresources used and the technological advances to convert them (NEVO for short term, WCO and WFO for the short to medium term, and algal oils, micro-and macroalgae for the medium to long term) (Fig. 29). The pre-concentration and *in situ* esterification/transesterification of micro-or macroalgae via supercritical bioethanol with the addition of CO<sub>2</sub> and integrated cogeneration (adding value to the residual algal biomass) are also a scientific and technological breakthrough. Moreover, the “biodiesel Sc-BioEt/CO<sub>2</sub>-TG” could be generalized as “biodiesel Sc-BioAlc/CO<sub>2</sub>-TG” where the bioethanol (BioEt) would be replaced by any other bioalcohol (BioAlc). Note that in BioD-SHE approach, the TG are already derived from non-edible lipid sources and represent also the constituents resulting from their partial decomposition, i.e. DG, MG, FFA and water.

Other aspects of the BioD-SHE alternative such as scientific & technological shortcomings, sustainable & innovative aspects, and

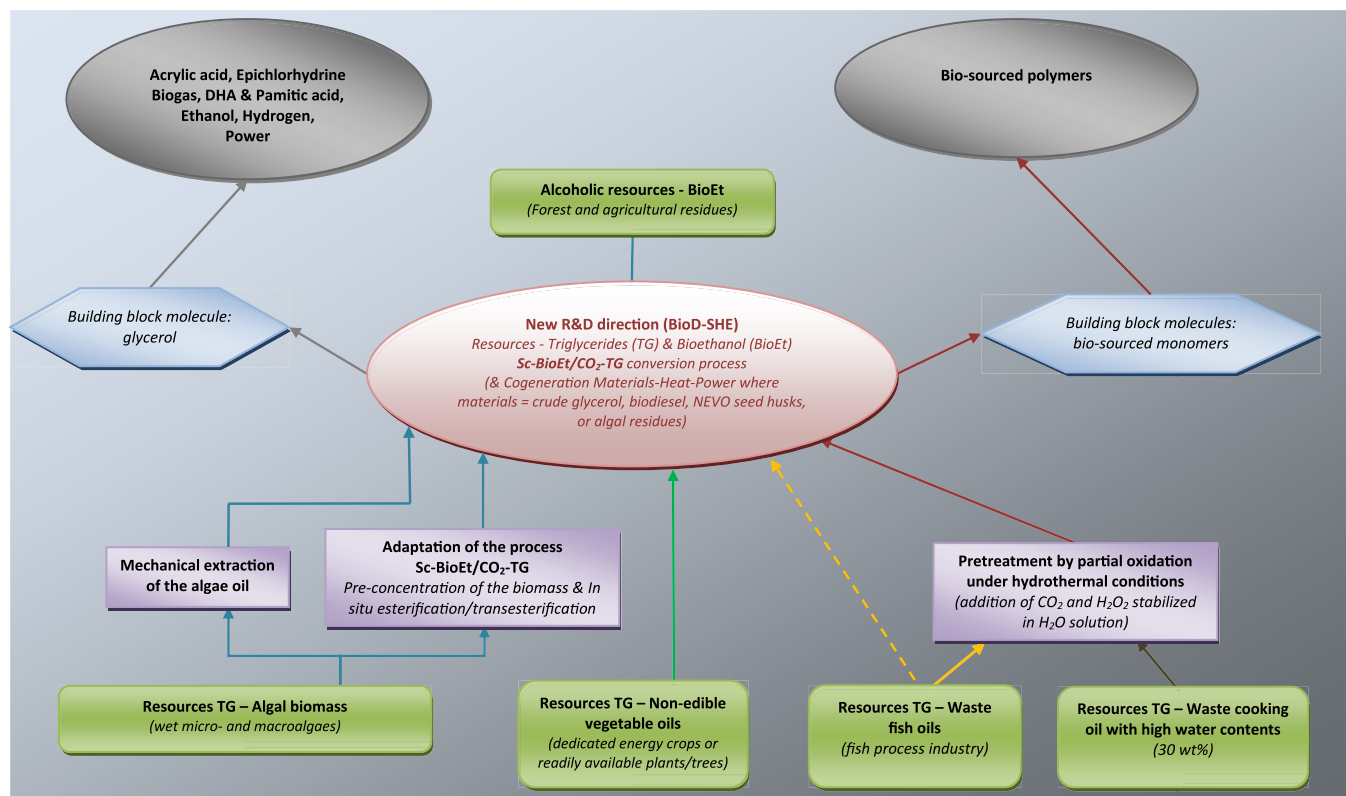


Fig. 29. Example of a new R&D direction (BioD-SHE): flexibility of the conversion process in terms of feedstocks and technology (coupling «biodiversity & techno-diversity»).

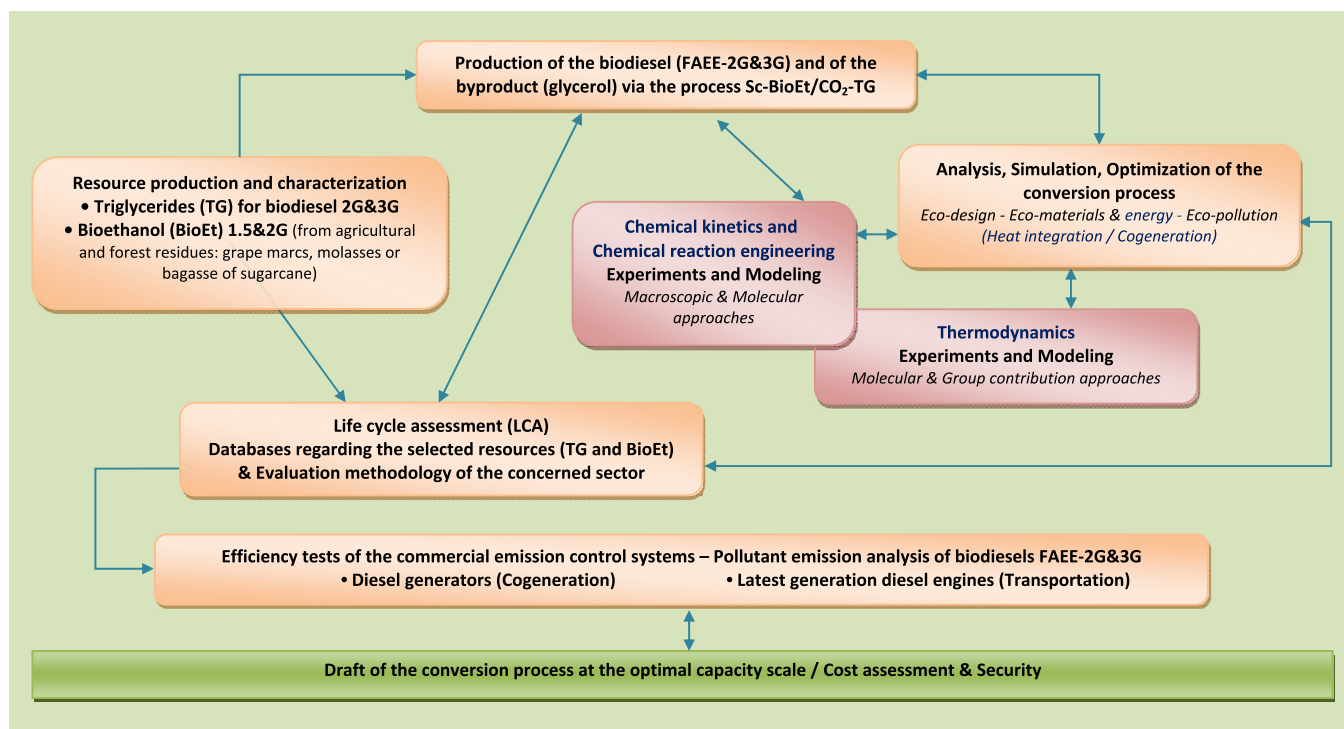


Fig. 30. Example of a new R&D direction (BioD-SHE): linkages between the various scientific and technical disciplines.

the benefits on the scientific, technical, industrial & economic fronts are mentioned in Table 4. Two of them require however further details.

- First regarding the sustainable and innovative aspects, it should be pointed out that resulting from the overall analysis of the sector, the combined formulation “process-product” offers various significant advantages. In addition to allow orientating the process specifications to produce a biofuel with the desired properties (Table 4), this approach also offers additional degrees of freedom during process simulation and optimization integrating LCA, and thus a safer convergence toward satisfactory solutions. These “degrees of freedom” are, for instance, acceptable levels of residual ethanol, water, or ethers derived from the

*in situ* conversion of glycerol. All these may simultaneously improve performance and emissions both at the level of the process and of the engine (as well as LCA of the entire sector). Indeed, there is no reason to include in the conversion process separation units to eliminate all the residual ethanol or water, from the biodiesel if this one is mixed afterward with ethanol or water to prepare a cleaner biofuel (without omitting energy savings which could be achieved). While these formulations are made in well defined specific proportions of the various constituents, they could be achieved by the process specifications.

- Secondly regarding industrial benefits within the context of microalgae exploitation, the BioD-SHE alternative would be located downstream to the microalgae production providing a way of converting their lipids on FAEE, using the light cuts for

Table 3

Potential alternatives for the cogeneration materials—heat—power and potential crude glycerol upgrading pathways within the new R&D direction suggested (BioD-SHE). Hydrated bioethanol 1.5&2G is used as alcoholic resource.

Lipid-based feedstock	Non-edible vegetable oil (NEVO)	Waste cooking oil (WCO, including frying and animal fats)	Pre-concentrated algal biomass (either dedicated to biodiesel production or light fractions of microalgae dedicated to pharmaceutical applications)
Materials used in the Cogeneration unit “Materials—Heat—Power”	Husk seed residues, straw	Part of the produced biodiesel	Algal residue post-ethanolysis via Sc-BioEt/CO <sub>2</sub> -TG (microalgae cells)
Crude glycerol upgrading pathway	Catalytic etherification at low temperature of glycerol in fuel additive suitable for diesel and biodiesel		Carbon source for algal fermentation producing DHA (diary complements) and palmitic acid (recycling into the feed for conversion in biodiesel)
	Conversion of glycerol in biohydrogen and bioethanol by microbial mixed culture		
	Supercritical water reforming of glycerol in hydrogen and power (reused in the reforming system for an energy self-sufficiency) – Recycling of water resulting from microalgae cultures after dewatering (for algal biomass feedstock)		
	Supercritical ethanolysis conducted with stoichiometric alcohol/oil ratio and high temperature (673 K) for a 100% conversion of oil in FAEE and of glycerol in ethers		



**Table 4**  
Scientific & technical shortcomings, sustainable & innovative aspects, scientific, technical, industrial and economic benefits of the new R&D directions suggested (BioD-SHE).

<i>Scientific and technical shortcomings</i>	
<ul style="list-style-type: none"> <li>Adaptation of the supercritical technology to the planned resources with integration of cogeneration “matter–heat–power”</li> <li>Development in a symbiotic way of the experimental and theoretical knowledge required as background for process simulation (laboratory and pilot scale) and optimization (industrial scale) with evaluation of the optimal production capacity confirmed via LCA</li> <li>Assessment of energy savings achieved through the implementation of the cogeneration unit, coupling efficient energy integration with reduced pollution</li> <li>Pollutant emission assessment from a vehicle operating under real conditions and from a power generator</li> </ul>	
<i>Sustainable and innovative aspects</i>	
<ul style="list-style-type: none"> <li>Propose a hybrid process combining the lipid biomass (terrestrial and aquatic) with thermochemistry as a conversion approach</li> <li>Use a multi-criteria approach to the global assessment validated by theoretical and experimental procedures, at the laboratory and pilot scale, in order to predict confidently the industrial scale by simulation and optimization using the “tools” of knowledge and methodology developed formerly</li> <li>Via an overall analysis of the sector, apply a combined “process–product” formulation offering the possibility to orientate the specifications of the process toward the desired properties of the produced biofuel (FAEE with possibly residual ethanol, water, and/or ethers)</li> <li>Integrate in assessment of the alternative “biodiesel Sc-BioEt/CO<sub>2</sub>-TG”, cogeneration “matter–heat–power” [326] and the glycerol valorization as output of the process, adapting them to the nature of the lipid resources (Table 3)</li> <li>Evaluate the effectiveness of existing pollution control systems of diesel engines in terms of specific biodiesel emissions both in power generators and vehicles</li> <li>Determine via the integrated approach “multi-scale modeling/simulation/experimental validation/optimization/LCA” the optimum capacity of the process in line with the chosen sector and propose the adequate option: “low capacity &amp; delocalized resources” or “high capacity &amp; centralized production centers”</li> </ul>	
<i>Scientific, technical, industrial and economic benefits</i>	
<ul style="list-style-type: none"> <li>On the scientific and technical aspects:               <ul style="list-style-type: none"> <li>Development of a comprehensive methodology for decision support to a sustainable alternative approach of biofuel production, integrating socio-techno-economic, environmental and safety impacts</li> <li>Development, adaptation or extension of theoretical physico-chemical models for the description of the systems involved in the process</li> <li>Development of devices and apparatuses for the generation of experimental data necessary to develop, validate or extend the physico-chemical models implemented in the softwares for process simulation and optimization with application to the production of 2G&amp;3G biodiesels (Table A.1., ESI)</li> <li>Development of “platform chemicals” (Fig. 29), i.e. the glycerol and bio-based monomers that may be produced via an alternative method “Sc-BioEt/CO<sub>2</sub>-TG” (Partial hydrothermal oxidation of TG in the presence of CO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> stabilized in water)</li> <li>Demonstration of the viability of an innovative process to produce 2G&amp;3G biodiesels (environmental-friendly process authorizing a wide range of resources)</li> <li>Demonstration of other applications of supercritical CO<sub>2</sub> conventionally used as extraction and fractionation solvent [187,328–337]</li> </ul> </li> <li>On the industrial side:               <ul style="list-style-type: none"> <li>Complementarity of BioD-SHE with industrial exploitation of microalgae</li> <li>Predictable interest of companies recollecting WCO and biofuel production companies using alternative resources (EcoMotion: 144,000 tons of methyl biodiesel produced in Europe from WCO in 2013)</li> <li>Contribution to the maintenance and development of SMEs</li> </ul> </li> <li>On the economic front:               <ul style="list-style-type: none"> <li>Decrease the cost of alternative fuels by using food wastes as a resource: WCO (containing non-negligible amounts of water) and hydrated ethanol (avoiding the very expensive last purification step to remove water)</li> <li>Contribution to the creation of rural jobs and energy independence in developing countries by giving them a technology friendly toward the individual and the environment, applying the biorefinery concept and using readily available agricultural resources</li> <li>Contribution to the positive image of chemistry reserving the noble resources to the food and health sectors and non-food resources to energy</li> </ul> </li> </ul>	

biodiesel production, while the heavy fractions would be used to pharmacology. In addition, glycerol byproduct could be used as carbon source for the microalgae harvest. Based on the concept of biorefinery, this option should improve even more the sector LCA.

## 11. Conclusions

It is regrettable that so far the supercritical ethanolysis of lipids with the addition of CO<sub>2</sub>, glycerol recovery and integration of a cogeneration mass–heat–electricity has not yet been realized at either a lab or pilot scale or virtually using an integrated approach “multiscale modeling/simulation/experimental validation/optimization/LCA”. The available scientific and technological building blocks, and the necessary developments, both experimental and theoretical, to evaluate this alternative before passing to a semi-industrial scale have been highlighted in this study.

On the basis of this analysis, a proposal for a new R&D direction aimed at developing a new BioDiesel alternative that would be Sustainable for Human and Environment (BioD-SHE) is here presented. This proposal is in accordance with a recent LCA review conducted by Milazzo et al. [312] regarding the past, present and future situation of *Brassica* biodiesels, which concludes that the future of biodiesel lies in the use of non-edible energy plants growing on degraded land (like *Jatropha*, *Neem* or *Desert date*) or requiring no land-use (such as algae). In addition, biodiesel feedstocks should be as diversified as possible, depending on geographical locations in the

world [20]. Extension of the potential feedstocks to WCO and fats (including waste fish oils) would be doubly efficient as it would solve pollution issues while contributing significantly to the energy resource pool. Furthermore, introducing hydrated bioethanol as alcohol in the biodiesel sector should enhance the viability of both liquid biofuels, particularly if they are developed within the biorefinery concept [6,24,338], and even better via cellulosic bioethanol once its production becomes commercially viable [44,312]. Hence, non-catalytic supercritical ethanolysis of TG, combined with “glycerol valorization” and “materials (feedstock residues/glycerol/biodiesel)–heat–power cogeneration” admitting all these feedstocks is thus a viable conversion process for reaching the objective of a sustainable biodiesel alternative.

In addition, this R&D line (BioD-SHE) would bring a significant contribution to the challenge issued by the United States Department of Energy aimed at developing alternatives for clean and efficient combustion of 21st century transportation fuels [339]. FAEE from 2G&3G biomass, using supercritical process (with integrated cogeneration and glycerol valorization), are a promising alternative, not only at the production stage, but also at the engine combustion stage, for a fuel generating lower emissions than the commercial methyl biodiesel. Furthermore, next-generation advanced compression-ignition combustion strategies (such as the Homogeneous-Charge-Compression-Ignition) that have proven to be successful fuel-flexible engine technologies combine ultra-dilute combustion and low-temperature-combustion (generating low NO<sub>x</sub> emissions), well-mixed fuel and air streams (avoiding soot



formation), and high efficiency (by operating under high pressures) [339–342]. The technology for shifting to ethyl biodiesel (with or without glycerol-derived ethers) from the production process to the engine is already available (except for microalgae that still require additional research). However, efforts will need to be focused on the development of models, integrating both kinetic phenomena and phase equilibria thermodynamics, which are necessary to simulate engine combustion under high pressures, moderate temperatures, and diluted medium [42]. The thermodynamic models based on a fully predictive approach that the new R&D line (BioD-SHE) aims at developing to simulate the FAEE production via the supercritical route would then be also useful for the FAEE combustion modeling. Hence, with respect to the DOE challenge, this new R&D direction (BioD-SHE) would contribute by proposing a combination of [new generation feedstocks–production process–alternative fuel & compatible engine technology] that would produce sustainable alternative fuels (i.e. maximizing energy and material efficiency while minimizing environmental and economical impacts).

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### Notation (acronyms and abbreviations used repeatedly)

2G	second-generation
3 <sup>E</sup>	«Eco-Design» & «Eco-Materials» & «Eco-Energy»
3G	third-generation
AP	atmospheric pressure
BioEt	bioethanol
CHP	combined heat power (cogeneration)
CO	carbon monoxide
CO <sub>2</sub>	carbon dioxide
COSMO-SAC	conductor-like screening model–segment activity coefficient
CPA	cubic-plus-association
DG	diglycerides
DNPH	2,4-dinitrophenylhydrazine
DOE	design of experiments
EOS	equation of state
FAEE	fatty acid ethyl esters
FAME	fatty acid methyl esters
FFA	free fatty acids
FID	flame ionization detector
GC	group contribution or gas chromatography
HC	total hydrocarbons
HP	high pressure
HPLC	high performance liquid chromatography
HT	high temperature
LCA	life cycle assessment
LHV	lower heating value
LLE	liquid–liquid equilibria
LP	low pressure
LT	low temperature
MG	monoglycerides
MP	medium pressure
MS	mass spectrometry
MT	medium temperature
NEVO	non-edible vegetable oil
NOx	nitrogen oxides
NRTL	non-random two-liquid theory
P	pressure
PAH	polyaromatic hydrocarbons

PM	particle matter
PPR78	predictive Peng–Robinson 1978
PR	Peng–Robinson
RSM	response surface methodology
SAFT	statistical associating fluid theory
Sc	supercritical
ScF	supercritical fluid
SRK	Soave–Redlich–Kwong
T	temperature
TG	triglycerides
UNIFAC	universal function activity coefficient
UNIQUAC	universal quasi-chemical theory
VLE	vapor–liquid equilibria
VLLE	vapor–liquid–liquid equilibria
WCO	waste cooking oil
WFO	waste fish oil
WS	Wong–Sandler

### Appendix A. Supplementary material

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.pecs.2014.03.001>.

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